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A laboratory study was conducted to evaluate the potential of selected grouts for controlling the percolation of leachates from hazardous solid waste landfills or hazardous waste ponds. In the course of the study, seven different grouts were subjected to permeability tests and four of the grouts were tested for their reactivity by an immersion type test. Eight different chemicals, some with two concentrations, and two real-site wastes were used as permeants in the permeability tests, and as liquids for the immersion baths.

Based on the comparision of permeability and reactivity test results, a scheme was proposed to correlate the permeability changes of grouts to the weight and consistency changes that may occur during their reactivity testing.

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REACTIVITY OF VARIOUS GROUTS TO HAZARDOUS WASTES AND LEACHATES

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory (HWERL) assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of state and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

One of the objectives of the research being conducted by the Land Pollution Control Division (LPCD) of HWERL is to develop methods of preventing contamination of groundwater by pollutants. Grouting of soil zones around solid and hazardous waste sites constitutes one method of creating a barrier to prevent contamination.

This report describes the development of test methodologies and equipment and the results of a three year study to evaluate the long-term resistance to percolation of grouted soils, using commercially-available and newly-developed grouts subjected to selected chemicals which cover the more common waste effluents of larger industries. Such performance data on the durability and permeability of grouted soils interacting with various waste leachates is necessary if grouts are to be considered for sealing hazardous waste sites.

This report will be of interest to all those involved in the disposal of solid and hazardous wastes and to those interested in the use of grouts as a remedial measure to prevent groundwater contamination. Specifically, the report will impact contractors and operators of disposal facilities, and university and research laboratories at the forefront of knowledge in the teaching/application of waste disposal, site remediation, and prevention of groundwater contamination.

For further information, please contact the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

A laboratory study was conducted to evaluate the potential of selected grouts for controlling the percolation of leachates from hazardous solid waste landfills or hazardous waste ponds. In the course of the study, 7 different grouts were subjected to permeability tests and 4 of the grouts were tested for their reactivity by an immersion type test. The 7 grouts used were (1) acrylate, (2) cement-bentonite (mix 1), (3) cement-bentonite (mix 2), (4) sodium silicate, (5) glyoxal-modified sodium silicate, (6) sodium aluminate-modified sodium silicate, and (7) urethane. The grouts were injected into natural sands and gravel and were first tested with water for their baseline permeabilities. Eight chemicals and two real-site wastes were used as permeants in the permeability tests, and as liquids for the immersion baths. They included acetone, aniline, cupric sulfate, ethylene glycol, hydrochloric acid, methanol, sodium hydroxide, xylene, real-site paint waste, and real-site refinery waste.

The acrylate, cement-bentonite (mix 2) and urethane grouts had low baseline permeabilities with water, ranging from 2.3×10^{-10} to 3.6×10^{-9} cm/sec. The remaining four grouts had baseline permeabilities higher than 1×10^{-7} cm/sec.

During permeability testing, the acrylate grout exhibited excellent resistance to the paint and refinery wastes and sodium hydroxide, performed satisfactorily with cupric sulfate, ethylene glycol and xylene, and was seriously damaged by aniline, acetone, hydrochloric acid and methanol.

The permeability of the cement-bentonite (mix 2) grout was tested with acetone, aniline, cupric sulfate, hydrochloric acid, methanol, and sodium hydroxide. With every one of these chemicals the permeability of the grout improved, ultimately reaching a practically impervious state.

The urethane grout maintained its low permeability with acetone, aniline, ethylene glycol, methanol, paint waste, and refinery waste, and it performed marginally well with cupric sulfate and hydrochloric acid. However, the urethane lost its low permeability with sodium hydroxide and xylene.

Based on the comparison of permeability and reactivity test results, a scheme was proposed to predict the permeability changes of a grout based on weight and consistency changes that may occur during reactivity testing.

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SECTION 1

INTRODUCTION

One of the major environmental problems facing the nation is the threat of contamination of groundwater from leaking hazardous waste landfills and leachate ponds. If a waste site is underlain by an impervious stratum then the most cost-effective remedy may be using a cutoff slurry wall curtain constructed around the site and keyed into the aquiclude. However, if there is no impervious stratum below the waste landfill then the remedy may be the construction of a bottom seal created by injection grouting, in conjunction with a vertical slurry wall curtain. Alternately, both the bottom seal and side curtain may be made by injection grouting.

Injection grouting has been used for many years for stabilizing soils, to provide cutoff curtains under dams (Terzaghi and Lacroix, 1964), for stabilizing tunnels, and more recently it was proposed for containment of hazardous waste (Spooner et al., 1982; Kitchens, 1980; Malone et al., 1985; May et al., 1985).

When constructing an impervious barrier by injection grouting under a waste site, the grout must thoroughly penetrate the soil, and after having expelled the waste from the voids, it must set and harden in the soil. In addition, the hardened grout must provide a durable, impervious seal even when permeated by hazardous leachate.

Presently, suspension grouts are the most often used grouts for cutoff construction. Examples of suspension grouts are cement, bentonite, and cement-bentonite. The chemical grouts are more expensive and therefore are less commonly used. The most popular ones are the sodium silicate, urethane, acrylamide and acrylate grouts. As a rule, the injection of suspension grouts is limited to soil deposits coarser than medium sand (Spooner et al., 1984), while some chemical grouts can penetrate even coarse silt. Of course, what soil deposit can be penetrated, and how well, will also depend on the time available for injection and the existing overburden pressure.

The purpose of this study was to test the permeability and resistivity of selected grouts with ten chemicals and determine if the grouts had the durability to withstand the typical environment below hazardous waste landfills or lagoons, and thus could be considered for horizontal seal construction.

The study was composed of six interrelated activities:

a) Selection of grouts suitable for injection grouting into medium sand or pea gravel, and potentially resistant to hazardous chemicals

b) Choosing chemicals that represent real-site hazardous liquid wastes
c) Developing laboratory techniques to make grouted permeability and reactivity samples
d) Develop or adapt laboratory permeameters and permeability apparatuses suitable for testing with chemicals
e) Testing the grout samples for their baseline permeabilities with water and for any changes in their permeabilities with the chosen chemicals
f) Testing the grout samples for their reactivity to longtime immersion in the chemicals

The test results are presented in plots. The permeability test plots show how certain grout-chemical combinations resulted in the deterioration of the permeability of the grout, while others resulted in little or no detrimental changes. The reactivity test plots show what effect chemical baths had on grout samples. Some combinations caused weight gains, others weight losses, and still others caused no changes. In addition, changes in sample consistency were observed. The combined analysis of the two tests resulted in correlations that allow prediction of permeability changes from reactivity test results.

SECTION 2

CONCLUSIONS

1. Three of the grouts tested had very low baseline permeabilities with water: acrylate ($k = 5.1 \times 10^{-10}$ cm/sec), cement-bentonite (mix 2) ($k = 2.3 \times 10^{-10}$ cm/sec), and urethane ($k = 3.6 \times 10^{-9}$ cm/sec). They are excellent candidates for hazardous waste barrier construction.

2. Four of the grouts tested had permeabilities with water that exceeded 1×10^{-7} cm/sec. They were the cement-bentonite (mix 1), sodium silicate, glyoxal-modified sodium silicate and sodium aluminate-modified sodium silicate grouts. These probably would not be considered for cutoff construction.

3. When tested for its permeability with the various chemicals, the acrylate grout exhibited excellent resistance to real-site paint waste, real-site refinery waste and a 25% solution of sodium hydroxide. It performed satisfactorily with a 20% solution of cupric sulfate, 100% ethylene glycol and reagent grade xylene. The reagent grade aniline, 100% acetone, 4N hydrochloric acid and 100% methanol were very detrimental to the permeability of this grout, causing increases of several orders of magnitude in its permeability. In contrast, when the 25% solution of sodium hydroxide was introduced into the grout sample, its permeability decreased. However, this may have been temporary since only 0.2 pore volume of flow took place with the sodium hydroxide, and the trend may have reversed itself with more flow, but only after a very long testing time.

4. The cement-bentonite (mix 2) grout was tested with six chemicals. The permeation of 100% acetone, reagent grade aniline, 20% solution of cupric sulfate, 4N solution of hydrochloric acid, 100% methanol and 25% solution of sodium hydroxide all caused the permeability of the grout to decrease from its baseline permeability with water to a practically impervious state, with the permeabilities approximately equaling 3×10^{-10} cm/sec. This occurred at elevated gradients and over many days of testing, but with small flows due to the low permeability of the samples. It is possible that after a very long time of testing, and a few pore volumes of flow, the permeability of cement-bentonite (mix 2) grout would begin to increase with one or more of the above chemicals. Overall this grout was the most promising in the test series.

5. The urethane grout remained quite impervious with the majority of the chemicals. Reagent grade aniline, 100% acetone, 100% ethylene glycol, 100% methanol, real-site paint waste, and real-site refinery waste all had only relatively minor to medium effects on the urethane grout samples. With

the 20% solution of cupric sulfate and 4N solution of hydrochloric acid the grout performed marginally, as its final permeability slightly exceeded 1 x 10^{-7} cm/sec. The most detrimental to the urethane grout were the 25% solution of sodium hydroxide and reagent grade xylene. The sodium hydroxide caused an increase of 4.5 orders of magnitude in the permeability of the grout. Overall, however, this grout behaved very well.

6. From the above summaries (3,4,5), it is concluded that the selection of a given grout is very much dependent on the predominant chemicals at a site, urethane grout, for example, being most suitable where acetone, aniline, and methanol are to be isolated. On the other hand, for sites with sodium hydroxide the use of acrylate or cement-bentonite (mix 2) grouts would be recommended.

7. The sodium silicate, glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate grouts were relatively pervious with water. However, these grouts were found to be resistant to chemicals. The sodium silicate was resistant to the permeation of 100% ethylene glycol, real-site paint waste, real-site refinery waste, and xylene. The glyoxal-modified sodium silicate resisted permeability increases with 20% solution of cupric sulfate and 25% solution of sodium hydroxide. The sodium aluminate-modified sodium silicate had small changes in permeability with 20% solution of cupric sulfate and reagent grade xylene. The following grout-chemical combinations caused 0.5 to 0.75 order of magnitude increases in the permeability of the respective grouts: sodium silicate with 100% acetone, glyoxal-modified sodium silicate grout with reagent grade xylene, and sodium aluminate-modified sodium silicate with 25% solution of sodium hydroxide.

8. The permeability of the sodium silicate and cement-bentonite (mix 1) grouts actually decreased from their baseline permeabilities with water when they were permeated by real-site paint waste and refinery waste. The decreases ranged from 0.25 to 1.75 orders of magnitude. It was observed that while the samples were tested with the above leachates, microorganisms grew in the feed lines, especially the ones carrying the real-site refinery waste. It is postulated that once the microorganisms reached the pores of the above grout samples, they started to plug the voids and caused a continuous decrease in the permeability of the samples. The practical consequence of this may be that microorganisms could be used at hazardous waste sites not only for the digestion of certain leachates, but also for plugging the voids and cracks in insufficient liners or grout barriers.

9. The effects of the concentration of chemicals on the permeability of the acrylate grout were varied. It was found from the limited data that the chemicals with reduced concentration, as compared to the ones with higher concentration, may have any of three effects on the permeability of the grout: a) it may make the increase in grout permeability smaller, or even negligible; b) it may cause approximately the same increase in permeability, only delay it; or c) it may cause approximately the same increase in permeability and at the same pore volume flow, without delay. For example, with 100% methanol the permeability of the acrylate grout increased by approximately 5.5 orders of magnitude, while the 25% solution of methanol caused practically no effect, even after 20 pore volumes of flow. On the other hand

both the 1N and 4N concentrations of hydrochloric acid caused essentially the same increase, and at the same pore volume flow, in the permeability of the acrylate samples. Furthermore, the ultimate permeability of the acrylate grout samples was the same with both the 20% and 10% solutions of cupric sulfate. However, while the samples with the 20% solution reached their ultimate permeability within 5 pore volumes of flow, the grout samples with the 10% solution reached the same ultimate permeability after 15 pore volumes of flow.

10. The different concentrations of chemicals had varied effects on the permeability of the urethane grout. For example, there were cases where a chemical with a reduced concentration caused almost the same increase in the permeability of the grout, and at the same pore volume flow, as its 100% concentration. On the other hand, with the 25% concentration of ethylene glycol the urethane grout samples did not show an increase in permeability, even after 7 pore volumes of flow, while the samples with 100% ethylene glycol exhibited more than 1 order of magnitude increases in their permeability.

11. Based on the above discussed permeability tests with various concentrations of chemicals, and on the tests with real-site paint waste and refinery waste which had relatively low concentrations of chemicals, it appears to these writers that there may be a threshold concentration for any one chemical below which it will not cause significant increases in the permeability of a given grout. Furthermore, if the concentration of the chemical exceeds the above threshold concentration, but is below 100% concentration, then it most likely will produce the same ultimate increase in the permeability of the grout as the 100% solution, but it could take many more pore volumes of flow of the lower concentrate.

12. Based on the quality of the results, it is concluded that the workmanship, test procedures, permeameters, and environmental boxes, especially in Phase III, proved to be of outstanding quality. In addition, the two environmental boxes provided a totally safe enclosure for conducting the permeability tests with the potentially hazardous chemicals.

13. It was observed in several tests with various chemicals and grouts, and for a given grout-chemical combination, that often the longer a sample stayed on water during its saturation period, the less increase in permeability it exhibited later on with the chemical (see sample AC-24 versus AC-28).

14. From many permeability tests on grouts with chemicals, it appears that equilibrium of permeability was often not reached within 2 pore volumes of flow with chemicals.

15. From the results of selected pairs of tests, it appears that variations in net confining pressures did not affect conclusively the ultimate permeability of the acrylate and urethane grouts. Two pairs of acrylate samples were permeated, one pair with 100% acetone (AC-43 and AC-42) and the other with 100% methanol (AC-45 and AC-34), at two different net confining pressures each (120.8 and 241.5 kPa, or 17.5 and 35 psi).

There were no significant differences between the ultimate permeabilities of the respective pairs of acrylate samples. It should be noted that the reactivity tests of acrylate samples in the above two chemicals resulted in the hardening of the samples, which may explain the insensitivity of the permeability samples to the difference in confining pressures.

One pair of urethane samples (UR-46 and UR-47) was permeated by reagent grade xylene, the other pair by a 25% solution of sodium hydroxide (UR-44 and UR-45). There were no differences in the ultimate permeabilities of the two urethane samples in sodium hydroxide. In the reactivity tests the urethane grout disintegrated in the sodium hydroxide bath, thus, in the permeability test samples, the very soft grout must have yielded and the sand structure was carrying the confining pressures. Therefore, the permeabilities of the samples were not affected by the confining pressures. The UR-46 and UR-47 urethane samples were permeated by reagent grade xylene. Even though the reactivity tests indicated that the samples hardened in xylene, the permeability tests show that the ultimate permeability of sample UR-46 was threefold lower than that of sample UR-47, where the net confining pressure on the former sample was twice as high as that on the latter. So out of the four pairs of samples only the last showed a positive effect of the confining pressure.

These tests were conducted on samples that either got hard or disintegrated. Had they been samples that became soft upon the permeation of chemicals, a much more pronounced effect of confining pressures would have been observed.

16. Concerning the effect of gradient, there was a slight increase in permeability of urethane grout with a higher gradient, and some grout-chemical combinations showed a slight to moderate decrease in ultimate permeability due to a lower gradient. Also, when some grout samples with set gradients reached their equilibrium permeability and their test gradients were dropped, their permeability often dropped too (see AC-44 with 10% cupric sulfate). However, from general observations of permeability data, it was concluded that the gradient of water or chemical flow had no pronounced effects on the ultimate permeability of most of the tested grouts with the range of gradients used.

17. It is evident from some permeability test plots that even during no flow periods the chemicals continue to deteriorate the grout matrix in the samples. An example of this is the permeability versus flow plot for sample AC-42, which was tested with 100% acetone. The stair-step nature of the curve resulted from the stopping and restarting of the permeation process. Each percolation stage was followed by a period of rest, generally one to seven days, during which the permeameter was shut down. The destructive effect of the chemical on the permeability of the grout was evident from the increase of the permeability upon each restart.

18. Based on the above discussion, it was concluded that the quantity of pore volume flow to equilibrium may not be the sole parameter to consider. The duration of percolation should also be considered. In other words, it is postulated that if a grout sample was subject to a high gradient flow of a

chemical and reached final equilibrium after "x" pore volumes of flow, then at a lower gradient flow, where the time of exposure of the grout to the chemical is greater per unit pore volume of flow, final equilibrium may be reached after less than "x" pore volumes of flow.

19. From the test data on the various grout-chemical combinations it appears that one may consider using either of two types of grouts for barrier construction. One suitable type of grout would be that which has perhaps a medium low equilibrium permeability, say 1 x 10^{-8} cm/sec with a chemical. The other grout would be a less conventional one, which was never tested to equilibrium because of its very low permeability. An example would be the cement-bentonite (mix 2) with 20% cupric sulfate. This grout had a permeability of 3 x 10^{-11} cm/sec at the conclusion of its test. It was practically impervious. Since the test was terminated before the permeability of the sample came to equilibrium, one does not know the equilibrium permeability of this sample with cupric sulfate. However, quick calculations show that using a 1.5 m (5 ft.) thick grout curtain in a field application, and assuming typical gradient conditions, it may take 30,000 years for the first drop of cupric sulfate to make its way through the curtain. So it is immaterial whether the cupric sulfate will or will not cause great increases in the permeability of the grout, since it actually will not get to penetrate, say in 50 years, more than about 2.5 mm (0.1 in.) of the 1.5 m (5 ft.) thick curtain.

20. The analysis of the reactivity tests, and the comparison of their results with that of the permeability tests, allowed these writers to propose a scheme that correlates the weight losses or gains, and the simultaneous consistency changes of the reactivity samples of a grout exposed to a chemical, to expected changes in its permeability when permeated by the same chemical. This may allow an engineer to make at least the preliminary selection of suitable grouts for a site by using reactivity tests in place of the more costly permeability tests.

SECTION 3

RECOMMENDATIONS

Based on the analysis and study of the permeability and reactivity test results, and the conclusions reached, the following recommendations are made for future study:

1. The search for better grouts and their permeability and reactivity testing should continue. The best candidates may be modifications of the urethane grout, the cement-bentonite grout, the micro-silica plus cement plus bentonite combination grout, and the modified sodium silicate grout. Further attempts should be made to improve the sodium silicate grout by reviewing the proportions of water used, and the quantity of plasticizer used in the cement-bentonite grout should be studied. It is also suggested that permeability and reactivity tests be initiated on phenolic and lignochrome grouts.

2. The cement-bentonite (mix 2) grout samples exhibited very low permeabilities with the chemicals, however, because of lack of testing time and available testing stations, not all test samples had replicates. It is recommended that more replicate testing be conducted on this grout.

3. More testing of the effect of concentration of chemicals on the permeability of grouts is needed. The existence of a threshold concentration, below which the permeability of a grout would not be affected detrimentally, should be explored for each chemical-grout combination.

4. More permeability test work is needed to study the effects of real-site leachates on the various grouts, since they usually have lower concentration of chemicals than those used in this study. Also the effect of the chemicals in real combinations should be checked. The tests with real-site leachates should be conducted over a long period to make sure that an equilibrium permeability is indeed reached.

5. The study of the effect of gradient on grout permeability should be continued. Specifically, there is a need to conduct some low gradient, long-term permeability tests with chemicals to simulate real-site conditions. The information would then be correlated with the results from the more standard laboratory tests which are conducted at much higher gradients.

6. Since the preceding tests on the effects of confining pressure on the ultimate permeability of grouts were conducted on grouts that became hard, no conclusive results were reached. It will be necessary to conduct new permeability tests with varying confining pressures on grouts that soften

with the chemicals, such as acrylate grout with real-site refinery waste, or urethane grout with acetone, to demonstrate that in an actual barrier application the high confining pressures can have a healing effect on a grout that is deteriorating due to a chemical.

7. With reference to reactivity tests, it is recommended that

a) more tests be conducted to improve the relationship between reactivity and permeability tests
b) make all reactivity samples without sand aggregates so that the true shrinkage of the grouts can be measured
c) measure size changes of reactivity samples, in addition to weight measurements
d) more accurately describe the consistency of the samples
e) take all measurements more often than outlined in the standard procedure, so that the occasional disintegration of a sample will not be missed
f) take temperature readings to detect chemical reactions
g) consider continuous stirring of the chemical bath during the test so that the erosive action of the flowing chemical in the permeability sample will be simulated in the reactivity test.

8. Investigate the changes in the permeability of grouts as a function of the length of time of exposure to chemicals in conjunction with the effects of accumulated pore volume flow of chemicals. An understanding of the relative effects of the two factors is needed for practical design purposes.

9. More work is needed to learn if the increased permeability of an existing barrier could be reduced by the application of microorganisms which would be washed into the pores of the grout and reduce its permeability. The practical details and feasibility of this remedy must also be investigated.

10. Establish a laboratory procedure that would simulate in-the-field grout mixing, and develop a grout injection process that will model field grouting conditions, including grout pressures, overburden pressures, soil density and degree of saturation. Also, in grouting a permeability sample, it is recommended that the grout be injected into the soil that is saturated with the waste to be used in the permeability test.

11. Standardize the permeability test procedure, such as type of permeameter, gradient, net confining pressure and backpressure.

SECTION 4

MATERIALS AND METHODS

This chapter will give detailed descriptions of the soils, chemicals, grouts and testing procedures that were employed during the several phases of this study. Specifically, the chapter will cover the following:

1) soils
2) grouts
3) grouting techniques
    a) permeability samples
    b) reactivity samples
4) permeameters and assembly of samples therein
5) permeability measuring apparatuses and testing methods
6) chemicals and hazardous leachates used
7) data processing

SOILS

The material into which the grout is injected should resemble soil since the objective of the study was to determine the ability of various grouts to withstand attack from hazardous wastes and leachates at underground disposal sites. A readily available, chemically inert material of consistent properties and a gradation compatible with the selected grout was needed. Sand is usually used. Spooner et al. (1982), in their paper study of the compatibility of grouts with hazardous wastes, found that sands over a relatively narrow gradation band had been used by other researchers, as noted in the following:

> Tallard and Caron (1977b) recommend sand with a gradation from 0.1 to 0.3 mm. Other studies have used sands with well-defined size ranges including Ottawa 20-30 sand (Borden, Krizek, and Baker, 1982), Number 20 Monterey sand (Vinson and Mitchell, 1972), and Number 20 and 16 Monterey sand (Clough et al., 1977).

A common dimension must be used to compare the above recommended sand sizes. Using sieve opening in millimeters, it is noted that the Ottawa 20-30 sand would be in the range 0.84 to 0.60 mm while the Number 16 and 20 Monterey sands would have particle diameters of 1.19 and 0.84 mm, respectively.

Two sands and one pea gravel were used as aggregates in this study of grout/chemical compatibility testing. A commercially available silica sand was chosen for use with the urethane, acrylamide, and acrylate grouts. A natural mason's sand (minus Number 30 sieve, less than 0.60 mm) from the

Cincinnati area was used in tests of the sodium silicate grouts. Pea gravel passing a U.S. Standard 3/8 inch sieve and retained on the 1/4 inch sieve (sieve openings of 9.51 and 6.35 mm, respectively) was used with the cement-bentonite (CB) grouts since the CB materials could not be successfully injected into the sand columns. The properties of these three soils are described in Figure 1 and Table 1. The two sands classify as poorly graded sands with little or no fines while the pea gravel classifies as poorly graded gravel according to the Unified Soil Classification System. A description of the Unified Soil Classification System and the various symbols used in this report is given in Table 2.

It is recognized that the chosen aggregates will not replicate any specific landfill substratum. The selected sands and pea gravel do, however, represent general earth materials. As noted by Larson and May (1983), "landfill substrata could vary considerably from the selected test sand in mineral composition and permeability, however, these variables are not expected to affect the grout-waste compatibility."

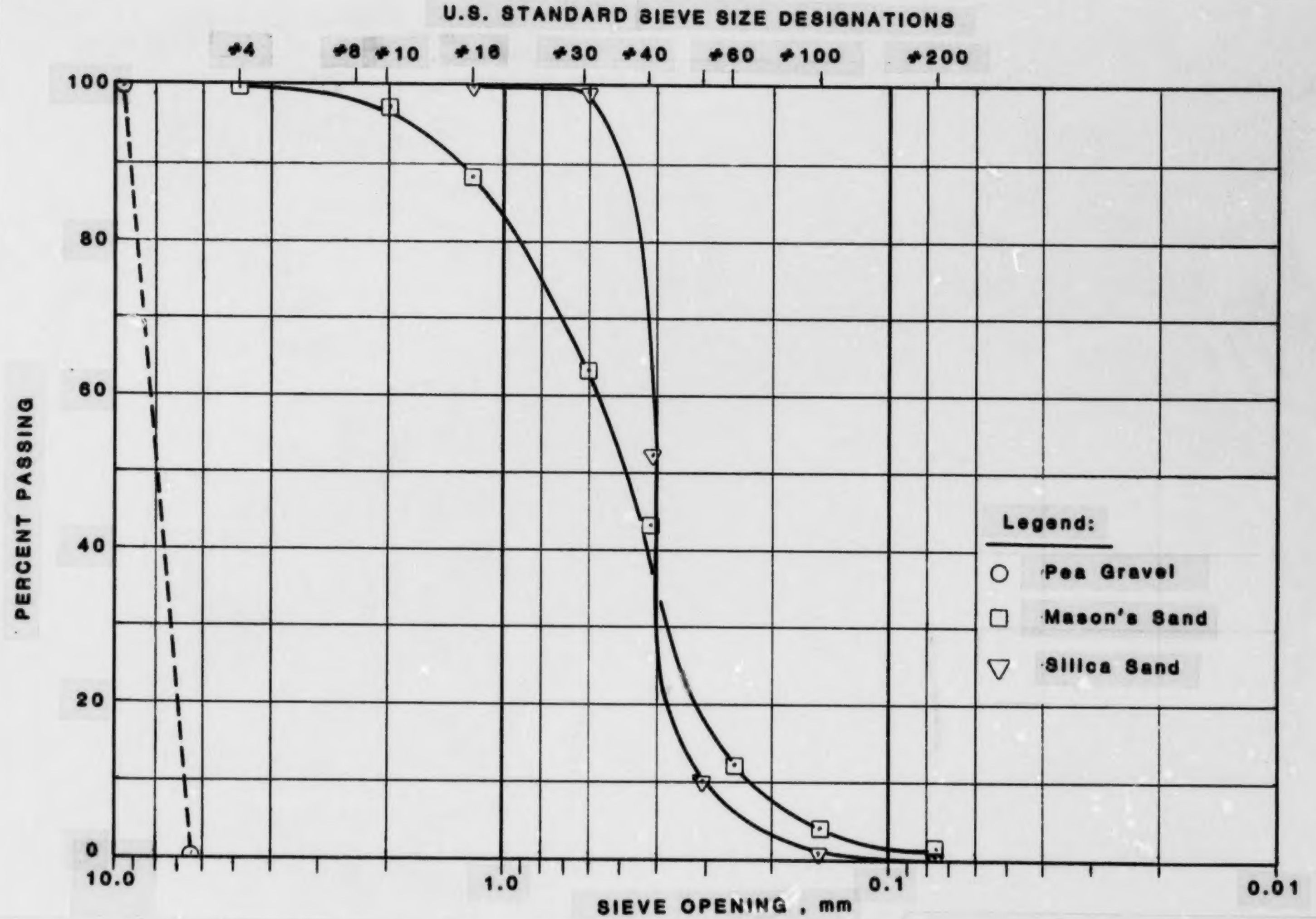

Figure 1. Grain size distribution curves for the soils used in this study.

TABLE 1. PROPERTIES OF THE SOILS USED IN PHASES I, II, AND III OF THE STUDY

Property	Silica Sand	Mason's Sand	Pea Gravel	Comments
Specific Gravity	2.63	2.74	-	
Optimum Moisture Content, %	3.3	14.0	-	
Maximum Unit Weight, kN/m^3*	16.5	17.2	-	via ASTM D698
" " " , pcf	104.9	109.2	-	
Minimum Void Ratio	0.52	0.50	-	
Maximum Void Ratio	0.68	0.70	-	
Coefficient of Uniformity, C_u	1.43	2.43	1.21	
Coefficient of Concavity, C_c	0.95	0.90	0.95	
Unified Soil Classification System Symbol	SP	SP	GP	

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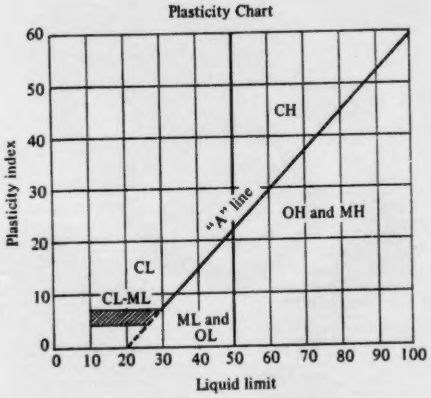
*kilo Newtons/m^3

TABLE 2. THE UNIFIED SOIL CLASSIFICATION SYSTEM

(ASTM D-2487)

Major Divisions			*Group Symbols*	*Typical Names*	*Laboratory Classification Criteria*		
Coarse-grained soils (More than half of material is larger than No. 200 sieve size)	Gravels (More than half of coarse fraction is larger than No. 4 sieve size)	Clean gravels (Little or no fines)	GW	Well-graded gravels, gravel-sand mixtures, little or no fines	Determine percentages of sand and gravel from grain-size curve. Depending on percentage of fines (fraction smaller than No. 200 sieve size), coarse-grained soils are classified as follows: Less than 5 per cent GW, GP, SW, SP More than 12 per cent GM, GC, SM, SC 5 to 12 per cent *Borderline* cases requiring dual symbols[b]	$C_u = \frac{D_{60}}{D_{10}}$ greater than 4; $C_c = \frac{(D_{30})^2}{D_{10} \times D_{60}}$ between 1 and 3	
			GP	Poorly graded gravels, gravel-sand mixtures, little or no fines		Not meeting all gradation requirements for GW	
		Gravels with fines (Appreciable amount of fines)	GM[a] d	Silty gravels, gravel-sand-silt mixtures		Atterberg limits below "A" line or P.I. less than 4	Above "A" line with P.I. between 4 and 7 are *borderline* cases requiring use of dual symbols
			u				
			GC	Clayey gravels, gravel-sand-clay mixtures		Atterberg limits below "A" line with P.I. greater than 7	
	Sands (More than half of coarse fraction is smaller than No. 4 sieve size)	Clean sands (Little or no fines)	SW	Well-graded sands, gravelly sands, little or no fines		$C_u = \frac{D_{60}}{D_{10}}$ greater than 6; $C_c = \frac{(D_{30})^2}{D_{10} \times D_{60}}$ between 1 and 3	
			SP	Poorly graded sands, gravelly sands, little or no fines		Not meeting all gradation requirements for SW	
		Sands with fines (Appreciable amount of fines)	SM[a] d	Silty sands, sand-silt mixtures		Atterberg limits above "A" line or P.I. less than 4	Limits plotting in hatched zone with P.I. between 4 and 7 are *borderline* cases requiring use of dual symbols
			u				
			SC	Clayey sands, sand-clay mixtures		Atterberg limits above "A" line with P.I. greater than 7	
Fine-grained soils (More than half material is smaller than No. 200 sieve)	Silts and clays (Liquid limit less than 50)		ML	Inorganic silts and very fine sands, rock flour, silty or clayey fine sands, or clayey silts with slight plasticity			
			CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays			
			OL	Organic silts and organic silty clays of low plasticity			
	Silts and clays (Liquid limit greater than 50)		MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts			
			CH	Inorganic clays of high plasticity, fat clays			
			OH	Organic clays of medium to high plasticity, organic silts			
	Highly organic soils		Pt	Peat and other highly organic soils			

Plasticity Chart

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[a] Division of GM and SM groups into subdivisions of d and u are for roads and airfields only. Subdivision is based on Atterberg limits; suffix d used when L.L. is 28 or less and the P.I. is 6 or less; the suffix u used when L.L. is greater than 28.

[b] Borderline classifications, used for soils possessing characteristics of two groups, are designated by combinations of group symbols. For example: GW-GC, well-graded gravel-sand mixture with clay binder.

(Source: Winterkorn and Fang, 1975.)

GROUTS

Background

The report by Spooner et al. (1982) concluded that "little actual chemical compatibility testing [had] been performed on grouts" and "few documented cases [existed] of the use of grouts and grouting technology for hazardous waste site remediation." Laboratory testing procedures or standards for grout/chemical compatibility had not been developed as of 1982. Their report was the impetus for this three-year program of study at the Environmental Protection Agency's Test and Evaluation Facility and the Center Hill Solid and Hazardous Waste Research Facility under contract to the University of Cincinnati. A companion study was conducted during the same period at the U.S. Army Corps of Engineers Waterways Experiment Station (WES) in Vicksburg, Mississippi (Larson and May, 1983; May et al., 1985).

Since the report by Spooner et al. (1982) was released, a number of researchers (JRB Associates, 1982; Larson and May, 1983; Lord et al. (not dated); May et al., 1985) have added needed information to the growing pool of theory, procedures, and results of grouting as a remedial action tool in hazardous waste leachate containment. Grouting took on a special significance following recent research (Anderson, 1982; Anderson and Brown, 1981; Anderson, Brown, and Green, 1982) indicating that various organic wastes, acids and other leachates could increase the permeability of clay liners. Flexible membrane liners (FMLs) have been used as barriers. FMLs are resistant to many chemicals, but they are subject to punctures, loss of elasticity, loss of seam strength, and are of limited life (Montague, 1982). Thus grouting appears to be a possible remedial action method for sealing the bottom of existing hazardous waste sites and for correcting leaks in FML systems.

Grouts have been used for years by the construction industry as a treatment method for soil and rock masses as either sealants or as stabilizing agents. Spooner et al. (1982) include an extensive review of the chemical and physical properties of the following grouts in their report:

bitumen
cement
clay
cement-bentonite
silicate
organic polymer (acrylamide, phenolic resin, urethane, urea-formaldehyde, epoxy and polyester grouts)
other miscellaneous grouts

Based upon the uses of grout in the construction industry, Spooner et al. (1982) found that "suspension grouts (cement, clay, and cement/clay) are the most common, accounting for approximately 95 percent of all grout used. Silicate grouts are the most commonly used chemical grouts, followed by acrylamide and urethane."

Spooner et al. (1982) noted that laboratory testing of grout/chemical compatibility centers on evaluating two general factors:

1) the effect of chemicals on grout set time, and
2) how long the grout will remain effective after prolonged exposure to the chemicals.

This study has focused primarily upon the second factor, and specifically has addressed the effect of hazardous wastes on the permeability and reactivity of various grouted soils.

When this study began, little information was available on the applicability of various grouts for the successful containment of hazardous waste leachates. Time and economics precluded the testing for compatibility of the thousands of grout/chemical combinations to be expected at disposal sites. Therefore, four grouts were chosen to provide the basis for this grout/chemical compatibility study--Portland cement with bentonite, sodium silicate, urethane and acrylamide. Because of the toxicity of acrylamide, it was later replaced by the non-toxic acrylate.

The same four basic grouts (with the exception of the bentonite additive) were chosen in the WES study. As summarized by Larson and May (1983) these grouts have the following properties:

> Cement: Cement grouts are suitable for rock and structures grouting, but are limited in soil (less than 0.1 mm diameter voids) grouting because the large particle size of the cement mixture reduces the permeability of the soil by plugging pore spaces. Although special agents may be added to prevent excessive water bleeding and alter the rate of setting, the problem of particle size still limits the use of cements. Water-cement ratio, degree of setting, and additives all affect the physical properties of cured and fresh cement (concrete). The properties of strength and durability are functions of time, temperature, humidity and compatibility with the material grouted (earth materials). Properties of the cement grout can be deliberately altered by mixing with other grout types such as acrylamide. The chemical compatibility data of cement grouts with various chemical compounds is not available in literature, however, the compatibility data of cement components with selected compounds is available. In general, cement grouts are compatible with hydroxides, weak alkali solutions, heavy metals, and neutral salts (JRB, 1982).
>
> Silicate Grouts: Silicate grouts, the second most commonly used, typically employ an alkali silicate, a gelling agent, and water. Gelling agents consist of acids, polyvalent cations, acid-forming compounds or selected organic compounds (Kirk-Othmer, 1979; Hurley and Thornburn, 1971). To enhance gelling, accelerators, such as chlorides, aluminates or bicarbonates may be used (Johnson, 1979). Organic esters may be used as a catalyst for retarding gelling time (Bowen, 1981). The viscosities of sodium silicate grouts vary from 1.5 to 50 centipoises (cP) and may be as high as 260 cP (Sommerer and Kitchens, 1980; and Tallard and Caron 1977a). Silicate grouts are subject to deterioration through syneresis, desiccation and solution erosion by ground water (Hurley and Thornburn, 1971). These properties and the varying grout mixture ratios can result in physical degradation such as fissure formation. Physical degradation

will then increase the surface area available to chemical degradation. Silicate grouts once gelled are resistant to moderate amounts of acids and alkali solutions (Kirk-Othmer, 1979).

Organic Polymer Grouts: The two types of grouts selected to represent this group are acrylamide and urethane grouts. The polymerization and crosslinking of these organic monomers forms an insoluble gel which is resistant to many waste chemicals. Acrylamide grouts consist of a monomer base, a crosslinking agent, an initiator and an accelerator.... With viscosities as low as 2 cP, the acrylamide grouts are capable of being injected into fine sediments.

Basic Grouts Tested

With this information as a general background, in-depth details of the grouts used and the modifications to the grouts that occurred over the period of study will be presented.

o Cement-Bentonite Grouts

Portland cement was selected on the basis of being the most commonly used grout in the construction industry despite its limited application in finer-grained soils. An unaltered bentonite (Wyo-bent) was added to the cement in order to fill the voids left in the hydrated cement. Initially, a mixture of 32.6% Type III cement (high early strength), 1.3% bentonite, and 66.1% water was used yielding a water-cement ratio of 2.0 (by weight) and a bentonite-cement ratio of 0.04. Tests performed using varying amounts of bentonite indicated that 4% bentonite was the optimum amount for water cutoff. Later, a superplasticizer (Mel-ment) was added to the grout and the water-cement ratio was reduced to 0.86. This significantly lowered the permeability of the grout while maintaining its fluidity. Pea gravel was used as the soil since the cement-bentonite mix could not be injected into the finer-grained sand.

o Sodium Silicate Grouts

SIROC 132, distributed by Raymond International Inc., was selected to represent the sodium silicate grouts . The non-toxic mixture consisted of 60% modified silicate (gel-forming material), 25% water, 10% formamide (gel-producing reactant), and 5% calcium chloride (accelerator). The gel time was rather flexible depending upon the mix design and temperature of the mix. Mason's sand (Figure 1) was selected as the soil to contain the sodium silicate grout. The choice of a fine-grained soil eliminated the problem of syneresis which can adversely affect the permeability of silicate grouts (Karol, 1982). Syneresis is the separation of liquid from a gel caused by contraction.

Later extensions to the sodium silicate work included a glyoxal-modified silicate grout and sodium aluminate-modified silicate grout. The glyoxal-modified silicate grout provides great flexibility in adjustment of gel times (American Cyanamid product literature). This feature, combined with the relatively low viscosity of the system, makes glyoxal-modified grout useful with fine soils such as sand where high penetration before gellation is important. American Cyanamid reports that by selection of appropriate glyoxal and calcium chloride levels, preliminary gel times of 4 to 50 minutes are possible. Gel time, of course, is affected by many factors including temperature and substrate composition.

Sodium aluminate was used as a replacement for the calcium chloride accelerator in some tests. Product information from the PQ Corporation indicated that the permeability of sodium silicate grout mixes using sodium aluminate would result in a lower permeability than when using calcium chloride as the accelerator.

∘ Urethane Grouts

CR360, a product of the 3M Company, represented the urethane chemical grouts. A mixture of 89.2% water, 5.7% CR361 (gel time extender), and 5.1% CR360 (hydrophilic urethane polymer solution) was used with a resulting gel time of 9 to 11 minutes at 20°C (68°F). The gel time could be extended to as much as 15 to 18 minutes by cooling the water to 7°C (45°F). Silica sand (Figure 1) was used as the soil to contain the grout.

∘ Acrylate Grouts

AC-400, distributed by Avanti International, was chosen to represent the acrylate grouts. A mixture of 73.44% water, 24.99% AC-400, 0.74% triethanolamine (TEA, catalyst), 0.74% ammonium persulfate (initiator), and 0.074% potassium ferricyanide (inhibitor) was used to obtain a gel time of approximately 40 minutes. This grout has a relatively low toxicity and low viscosity, making it suitable for its use in fine-grained soils. AC-400 was chosen to replace its acrylamide counterpart, which in its powdered, ungelled form, is a neurotoxin. As with the urethane grout, silica sand (Figure 1) was used as the soil.

Typical Mix Designs

This section presents the step-wise nature of the grout preparation. Because of the short gel time for many of the grouts used, experience and preparation are key issues. It is hoped that by including this section other researchers will avoid the trouble of trial-and-error approaches with these grouts in particular. The amounts given furnish approximately 3000 ml of grout in each case. Clean-up in all cases involves the use of copious amounts of water.

Common laboratory equipment is all that is required for the grouting operations. Typically one would use the following: stirring rods, a blender, a thermometer, beakers (through a full range of sizes), balance, tamping tools, a funnel, crescent wrenches, a stopwatch, Bunsen burner and its associated hardware, gloves, tongs, and plastic wrap. In addition, supplies of deionized water, carbon dioxide, pressurized air, and cleanup water are needed.

- Cement-bentonite (mix 1) grout

  - Components

    aggregate: pea gravel passing 3/8 inch sieve, retained on 1/4 inch sieve (6.4 to 95 mm)

Type III cement	3000 g
water, deionized	6000 ml
bentonite	120 g

  - Preparation

    a) mix the bentonite with 3000 ml of deionized water, then allow the mixture to sit for 48 hours

    b) mix (a) with the remaining 3000 ml of water and the cement in a blender for at least one full minute

  - Results

    a) water-cement ratio = 2.0

    b) set time = approximately 2 days

    c) grouted in molds using an air pressure of approximately 138 kN/m^2 (20 psi)

- Cement-bentonite (mix 2) grout using MC-500 microfine cement, bentonite, and dispersant

  - Components

    aggregate: sand passing Number 4 sieve, retained on Number 8 sieve (2.38 to 4.76 mm)

MC-500 microfine cement	3000 g
water, deionized	2250 ml
bentonite	120 g
NS-200 dispersant	30 ml

  - Preparation

    a) mix the bentonite with 1200 ml of deionized water, then allow the mixture to sit for 48 hours

    b) mix the remaining water with the NS-200 dispersant

    c) add the cement to (b)

    d) add (a) to the (b + c) mix and thoroughly mix in a blender for one full minute

  - Results

    a) water-cement ratio = 0.89

    b) set time = approximately 2 days

    c) grouted in molds using an air pressure of approximately 138 kN/m^2 (20 psi)

- Sodium silicate grout--standard SIROC No. 132

  - Components

aggregate: Mason's sand (minus Number 30 sieve, less than 0.60 mm)	
sodium silicate (SIROC #1)	1800 ml
formamide (SIROC #2)	300 ml
calcium chloride (SIROC #3) solution	150 ml
water, deionized (approx. 7°C, 45°F)	750 ml

  - Preparation

a) to prepare the calcium chloride solution, mix 9.3 g of calcium chloride with 150 ml of deionized water

b) into the cold deionized water mix the formamide; following this add the calcium chloride solution and agitate until mixed

c) in a separate container pour the sodium silicate and begin stirring

d) with the contents of (c) stirring rapidly, pour the solution from (b) into (c) [never in reverse order, as gelling will take place instantaneously] and stir continuously for one minute

  - Results

a) gel time = 15 minutes at 29.4°C (85°F)

b) gel time = 50 minutes at 20°C (68°F)

c) grouted in molds using an air pressure of approximately 55 kN/m^2 (8 psi)

- Glyoxal-modified sodium silicate grout
  - Components

aggregate: Mason's sand (minus Number 30 sieve, less than 0.60 mm)	
sodium silicate	1200 ml
glyoxal	120 ml
water, deionized (approx. 7°C, 45°F)	1680 ml
calcium chloride	13.95 g

  - Preparation

a) mix the calcium chloride accelerator with the cold water. A blender may be required depending upon how readily the calcium chloride dissolves

b) mix the glyoxal into the calcium chloride and water solution

c) while the sodium silicate is being constantly agitated (in a blender), pour in the mix from (b) and mix thoroughly for one minute

  - Results

a) gel time = approximately 20 minutes

b) grouted in molds using an air pressure of approximately 55 kN/m^2 (8 psi)

- Sodium aluminate-modified sodium silicate grout
  - Components

aggregate: Mason's sand (minus Number 30 sieve, less than 0.60 mm)

sodium silicate	1200 ml
formamide	180 ml
water, deionized	1362 ml
sodium aluminate	240 ml

- Preparation

a) mix the sodium aluminate into the deionized water

b) thoroughly mix the formamide into the solution from (a)

c) while the sodium silicate is being constantly agitated (in a blender), pour in the mix from (b) and thoroughly mix for one full minute

- Results

a) gel time = approximately 6 hours

b) grouted in molds using an air pressure of approximately 55 kN/m^2 (8 psi)

- Urethane grout
  - Components

aggregate: silica sand (minus Number 30 sieve, less than 0.60 mm)	
CR361 (gel time extender)	17.8 g
CR360 (hydrophilic urethane polymer solution)	156.96 g
water, deionized (approx. 7°C, 45°F)	2736.0 ml

  - Preparation

    a) pour the cold water into the gel time extender (CR361) and mix thoroughly

    b) pour the solution from (a) into the urethane and mix vigorously for one minute

  - Results

    a) gel time = 15 to 18 minutes when cold water (7°F, 45°F) is used; the gel time may be no more than 9 to 11 minutes if water at 20°C (68°F) is used

    b) grouted into molds using an air pressure of approximately 41.5 kN/m^2 (6 psi)

- Acrylamide grout
  - Components

aggregate: silica sand (minus Number 30 sieve, less than 0.60 mm)

water, deionized	2660 ml
AV 100 grout	300.3 g
triethanolamine (TEA, catalyst)	14.04 g
potassium ferricyanide (inhibitor) of nominal 10% stock solution	10.53 g
ammonium persulfate (initiator)	14.97 g

  - Preparation

a) mix ammonium persulfate in a beaker containing 1330 ml of deionized water

b) in a second beaker mix the AV 400 grout, TEA, and potassium ferricyanide solution with the remaining 1330 ml of water

c) pour (a) into (b) and mix vigorously for one minute

  - Results

a) gel time = approximately 5 to 12 minutes

b) grouted into molds using an air pressure of approximately 34.5 to 41.5 kN/m^2 (5 to 6 psi)

  - Caution

Acrylamide, in its powdered form, is a neurotoxin; no exposure should be permitted.

This grout was replaced by the non-toxic acrylate grout.

- AC-400 acrylate grout
  - Components

aggregate: silica sand (minus Number 30 sieve, less than 0.60 mm)	
water, deionized	2222 ml
AC-400 grout	756 g
triethanolamine (TEA, catalyst)	22.5 g
potassium ferricyanide (inhibitor)	2.25 g
ammonium persulfate (initiator)	22.5 g

  - Preparation

    a) mix ammonium persulfate in a beaker containing 1497 ml of deionized water

    b) in a second beaker mix the AC-400 grout, TEA, and potassium ferricyanide inhibitor with the remaining 725 ml of water

    c) pour (a) into (b) and mix vigorously for one minute

  - Results

    a) gel time = approximately 40 minutes

    b) grouted into molds using an air pressure of approximately 34.5 to 41.5 kN/m^2 (5 to 6 psi)

GROUTING TECHNIQUES

Preparation of Permeability Samples

- Selection of Test Methods for Determining the Effects of Chemicals on the Durability of Hardware Materials Used in the Testing Program

The hardware used to grout and to conduct permeability tests on the samples had to be durable and resistant to attack from grouts and leachates. In order to ascertain reactivity data on specific potential materials with the chosen leachates, American Society for Testing and Materials (ASTM) reactivity tests were conducted. ASTM Standards, D 543, "Test for Resistance of Plastics to Chemical Reagents" was used for all plastics and synthetic rubbers under consideration. ASTM Standards, G 31, "Standard Recommended Practice for Laboratory Immersion Corrosion Testing of Metals" was followed for all potential metals. During Phase I the reactivity and corrosion tests on potential hardware materials resulted in a list of materials that were judged unaffected by xylene, methanol, and acetone. These materials were Nylon 11, polytetrafluoroethylene (Teflon), dense polypropylene, aluminum (6061), stainless steel and brass. Materials allowed if not in contact with xylene, methanol, or acetone were latex, neoprene, and acrylic. As Phases II and III were conducted and other leachates were introduced, further reactivity testing was completed. Most of the decisions concerning material reactivity were based on information available in resistivity tables. Table 3 lists the resistance to corrosion of the various metals and plastics used as a function of the various leachates and concentrations thereof.

- Grouting Apparatus and Procedure

The soil samples were grouted in a 76.2 mm (3 in.) inside diameter plastic mold. Sample lengths could be varied as required, and several samples could be grouted within a single mold. The mold was made of 6.4 mm (0.25 in.) thick clear acrylic. Specifically, a 305 mm (12 in.) long grout cylinder was sawn longitudinally into two sections and a 3.2 mm (0.125 in.) diameter groove was machined down each cut face. A 3.2 mm (0.125 in.) diameter rubber seal was placed in the groove and five hose clamps were used to hold the cylinder together and compress the seals (see Figure 2). Two aluminum endplates, each with a recessed center portion to accept the cylinder ends, were used as base and cap for the mold. A seal was provided by rubber gaskets at the top and bottom. Brass valves were fitted into the center of each endplate for introduction of the grout from below and metering and exhaust of the outflow at the top. The cylinder and endplates were compressed longitudinally with three threaded rods and wingnuts. A lecithin mold releasing agent was sprayed on the inside of the mold to facilitate sample removal.

Several methods were used to prepare the soil samples for grouting. In Phases I and II the chosen sand was dropped 200 mm (8 in.) from a funnel to form 25.4 mm (1 in.) thick lifts in the cylindrical mold. Each lift was rodded 25 times with a 9.5 mm (0.375 in.) diameter rod, using care not to enter previously compacted layers. A round bar with an end area of 968 square mm (1.5 sq. in.) was used to level out the top of the sand when the desired sample thickness was reached.

TABLE 3 CORROSION RESISTANCE CHART FOR THE HARDWARE USED FOR THE GROUTING AND PERMEABILITY TESTING EQUIPMENT

LEACHATE	Chemical Concentration Percent	Aluminum	Brass	Monel	Stainless Steel	Titanium	PVC	Teflon
Acetone	100	E	G	E	E	E	U	R
	25	E	G	E	E	E	U	R
Aniline	100	G	U	G	E	E	U	R
Cupric Sulfate	20	U	U	S	G	E	R	R
	10	U	U	S	G	E	R	R
Ethylene Glycol	100	G	G	G	G	-	R	R
	25	G	G	G	G	-	R	R
Hydrochloric Acid	50	U	U	U	U	E	R	R
	25	U	U	U	U	E	R	R
	10	U	U	G	U	E	R	R
Methanol	100	G	G	G	G	G	R	R
	25	G	G	G	G	G	R	R
Sodium Hydroxide	50	U	U	E	E	U	R	R
	25	U	G	E	E	U	R	R
	10	U	G	E	E	U	R	R
Xylene	100	G	G	G	G	E	U	R

Explanation

For Metals:

E = < 2 Mils penetration/year
G = < 20 Mils penetration/year
S = < 50 Mils penetration/year
U = > 50 Mils penetration/year

For Non-metals:

R = Resistant
U = Unsatisfactory

Temperature range: 16 to 38°C (60 to 100°F)
Reference: Modified from Brady (1977)

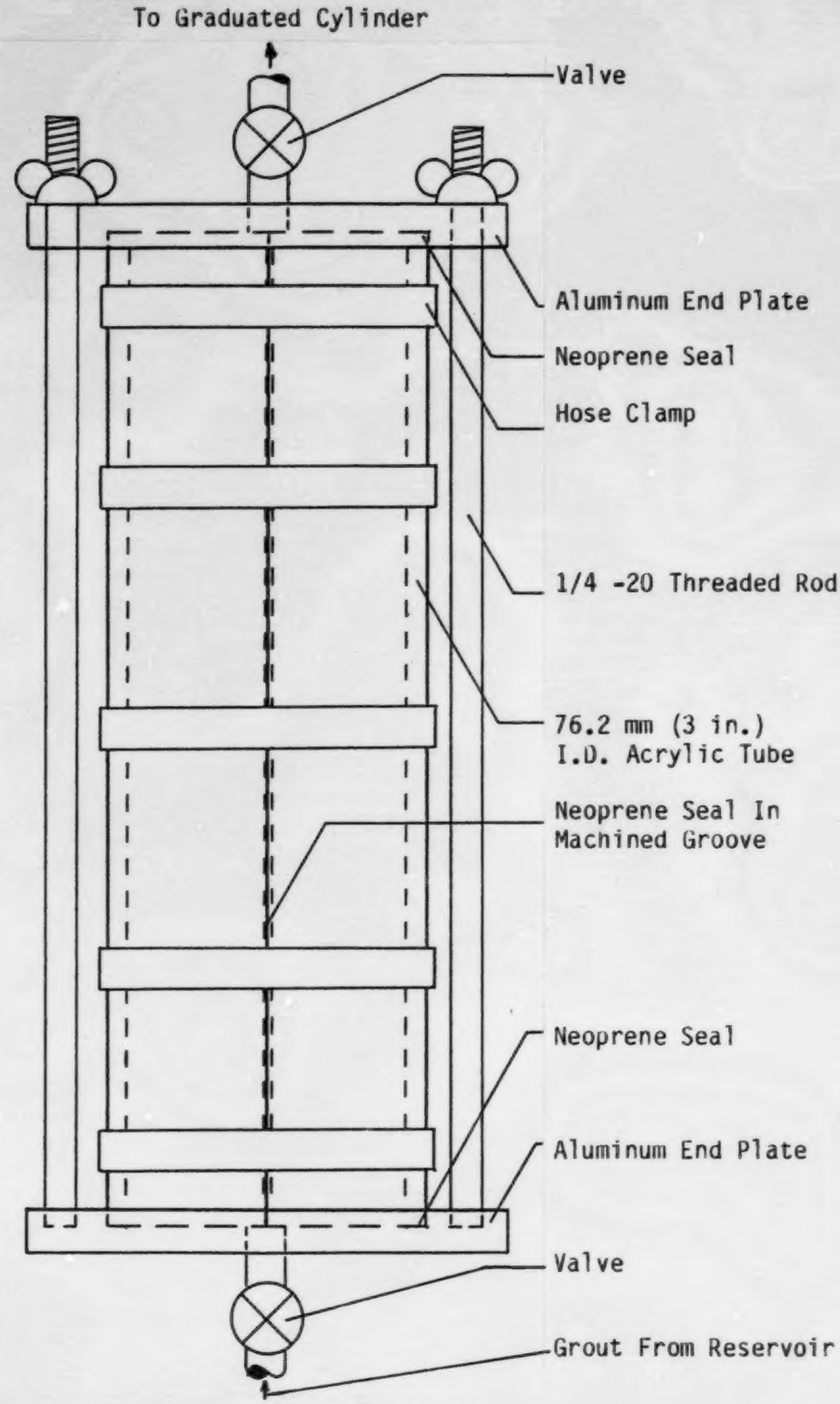
To Graduated Cylinder
Valve
Aluminum End Plate
Neoprene Seal
Hose Clamp
1/4 -20 Threaded Rod
76.2 mm (3 in.)
I.D. Acrylic Tube
Neoprene Seal In
Machined Groove
Neoprene Seal
Aluminum End Plate
Valve
Grout From Reservoir

Figure 2. Details of the grouting mold used to prepare permeability samples.

In Phase III the sand and pea gravel layers were compacted in 38 mm (1.5 in.) lifts using a plastic tamping tool 305 mm (12 in.) long with 38 mm (1.5 in.) square hardened end plates. Each lift was surface tamped 25 times. In all phases rigid, perforated plastic disks were placed at the top and bottom of each sample to ease separation and to provide flat and square ends. This action also eliminated the need to saw the samples and the possible inducement of distress into the samples during the cutting process.

Generally, five or six samples 38 mm (1.5 in.) in height could be produced in a mold. The molding process allowed for a waste sample 25.4 mm (1 in.) thick at each end of the mold. Some samples were cast 76.2 mm (3 in.) thick, particularly those for which a high coefficient of permeability was expected. Following the preparation of the soil, the pressure resistant mold was capped and a carbon dioxide line was attached to the bottom of the cylinder. Carbon dioxide, heavier than air, was passed through the soil at 13.8 kN/m^2 (2 psi) to displace all air from the voids. Air left in the soil voids can affect the permeability of grouted samples; it is also difficult to reproduce the same degree of saturation in many samples if all the void air is not replaced by water.

Next, deaired and deionized water was passed through the carbon dioxide-saturated soil, using a pressure of 70 kN/m^2 (10 psi) from beneath. Forcing the gas ahead of it, the water took on the remaining carbon dioxide in the pores to form a dilute carbonic acid. This left the voids nearly gas-free and almost perfectly saturated with liquid. Six pore volumes of water were passed through the sample to displace the weak carbonic acid and flush it from the voids. The flow was metered so that quick conditions did not arise in the soil.

At this point the grout tank was attached to the bottom of the mold (see Figures 3 and 4). The grout tank was located between the regulated air source and the grouting mold. The grout tank was a reservoir that stored the premixed grout. It was connected directly to the grouting mold via 6.35 mm (0.25 in.) flexible polyvinyl tubing. For flow control purposes the tank was equipped with a 6.35 mm (0.25 in.) NPT x 6.35 mm (0.25 in.) TUBE brass plug valve that was fastened to the bottom endplate. The top endplate was fitted with a 12.7 mm (0.5 in.) NPT x 12.7 mm (0.5 in.) TUBE nylon connector to receive the air line. Each endplate consisted of a 19 mm (0.75 in.) thick by 203 mm (8 in.) diameter acrylic sheet. The tank consisted of a 152.4 mm O.D. x 305 mm x 12.7 mm (6 in. O.D. x 12 in. x 0.5 in.) wall thickness acrylic tube machined and fitted on each end with a 3.2 mm (0.125 in.) diameter neoprene gasket seal. Four 6.35 mm (0.25 in.) x 20 threaded steel rods with associated hex nuts and washers completed the assembly. The liquid grout was injected at a pressure and flow rate suitable for each grout mix and the chosen soil (as noted in the section on mix designs). In order to replace all the water in the voids, at least two soil pore volumes of grout were passed through the sample before closing the valves to the mold and starting the curing process. Curing typically required two days in the mold, then seven or more days wrapped in plastic film in a controlled environment at approximately 98 percent humidity and 20°C (68°F).

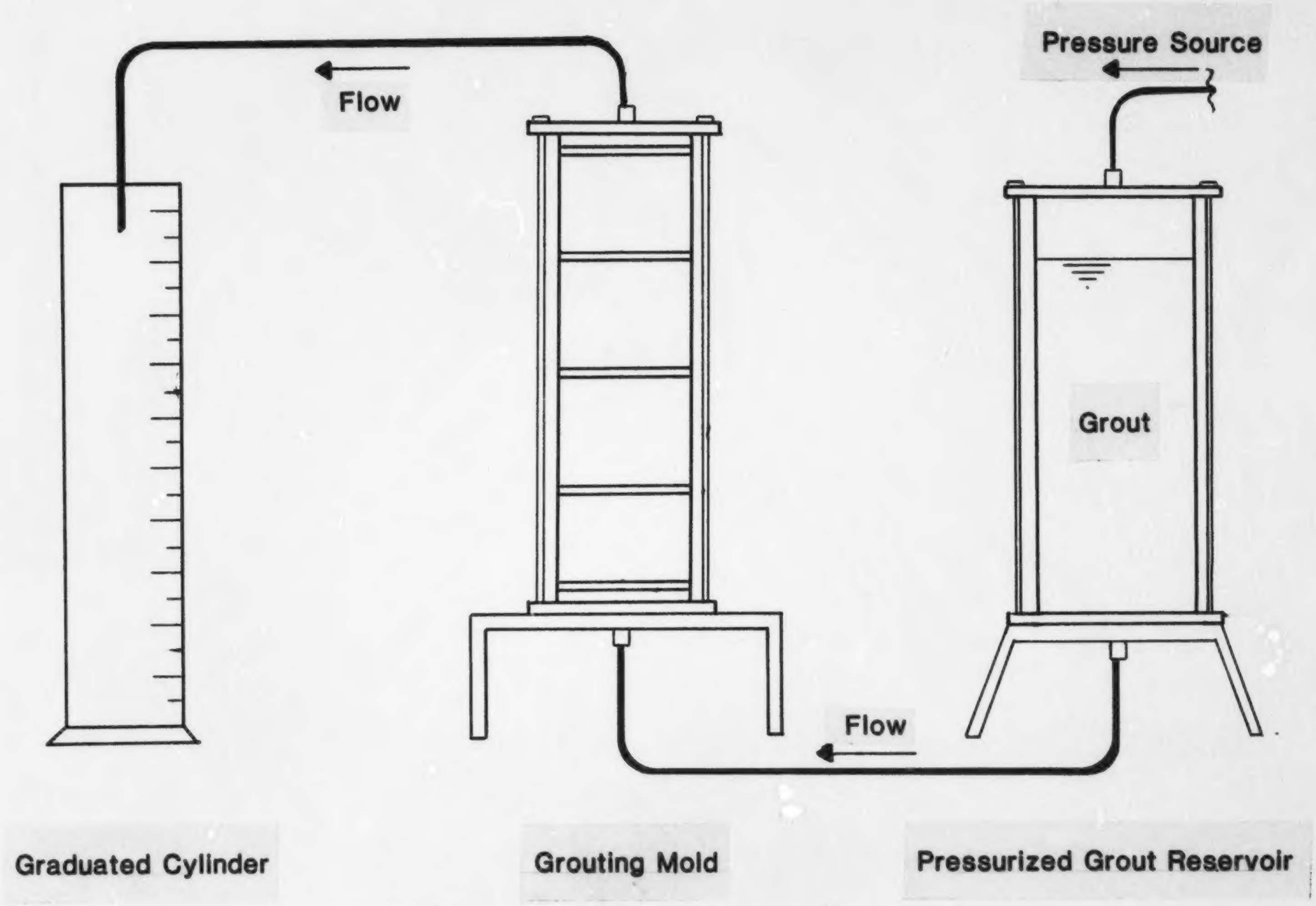
Pressure Source
Flow
Grout
Flow
Graduated Cylinder
Grouting Mold
Pressurized Grout Reservoir

Figure 3. Schematic drawing of the grouting system.

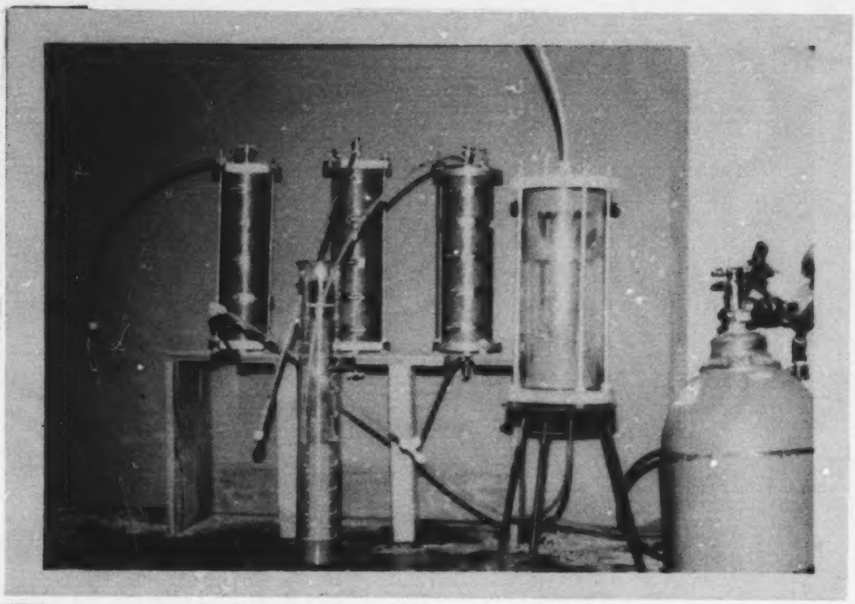

Figure 4. Grouting system consisting of a pressurized grout tank, grouting molds, a graduated cylinder, and air and carbon dioxide sources.

Preparation of Reactivity Samples

The testing technique for obtaining the approximate reactivity of the grouted soils to leachates underwent extensive changes over the three phases of the study. In the early stages of Phase II, immersion tests were conducted according to ASTM Standard D 543, "Test for Resistance of Plastics to Chemical Reagents." To prepare the immersion coupons, the liquid grout was mixed with the sand by hand and placed in 6.4 mm (0.25 in.) layers in a 38 mm (1.5 in.) diameter tube, each layer being separated by two filter papers. After 48 hours of curing in the mold, the samples were removed and placed in a controlled environment at approximately 98 percent humidity and 20°C (68°F) for four days before measuring, weighing and immersion in the chemicals. Each specimen was placed in 150 ml of one of the three chemicals used in Phase I, i.e., xylene, methanol, or acetone. The samples were swirled and visually checked daily for seven days. After that, they were towel-dried, weighed and measured.

As one of the objectives of the laboratory testing of the grout/chemical compatibility was to evaluate the durability of grouted soils after prolonged exposure to the chemicals, the reactivity tests were modified for Phases II and III. In the latter two phases the reactivity samples were grouted in a new mold. The mold was made of clear acrylic 25.4 mm (1 in.) thick, 102 mm (4 in.) wide and 610 mm (24 in.) long with twelve 25.4 mm (1 in.) thick diameter holes drilled completely through. The bottom was lightly coated with oil and secured to another acrylic sheet (see Figure 5). The oil provided a seal between the two acrylic sheets, essentially preventing any grout from leaking.

The resulting samples in Phases II and III were prepared by first placing the soil in the molds and tamping the surface to provide some densification of the sand. In order to force the air from the voids the grout was injected slowly and continuously from the bottom of each sample using a syringe (see Figure 5). The injection process continued until a liquid sheen appeared over the entire surface of the sample. It should be noted that the cement-bentonite reactivity samples were prepared using no aggregate due to the size of the pea gravel relative to the molds. Figure 6 depicts the preparation of the cement-bentonite reactivity samples by spooning the grout into the mold. Three replicate samples were prepared for each grout/chemical combination. The samples were cured following the procedure outlined for the reactivity samples in the early stages of Phase II. Basically ASTM Standard C267-82 "Standard Test Method for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings" was followed for the preparation of the grouted samples. The same standard was followed for guidance on the weighing, measuring and immersion of the specimens. Observations and weighings were made after 1, 7, 14, 28, 56, and 84 days of immersion. Plots were made illustrating the percent change in weight (as compared to the initial weight) versus time for each sample and replicate series.

The reactivity samples were immersed in chemicals in beakers which were labelled and covered to reduce evaporation within an exhaust hood (see Figures 7 and 8). Aluminum foil was originally used as the cover but the foil was destroyed in the chemical atmosphere. The foil was replaced by Parafilm "M"

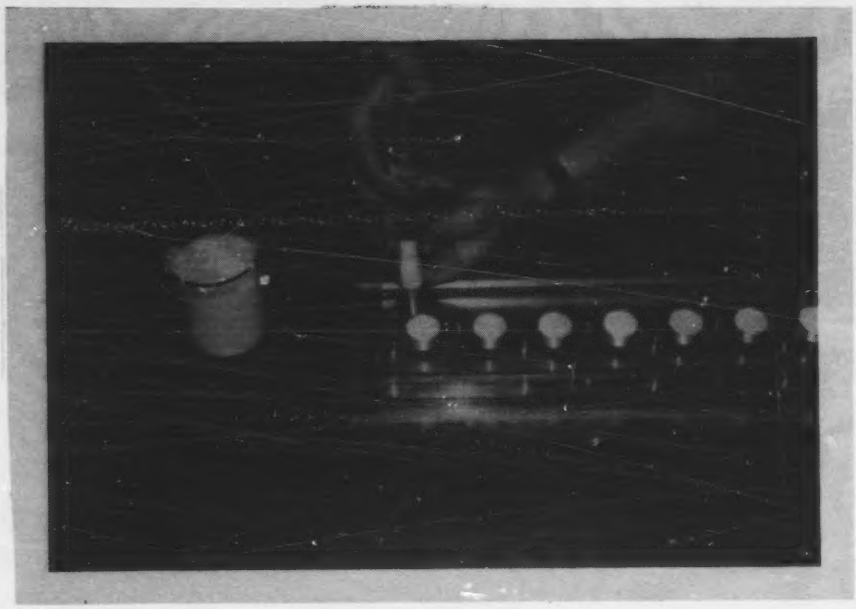

Figure 5. Preparation of reactivity samples using a syringe to inject the grout into the soil.

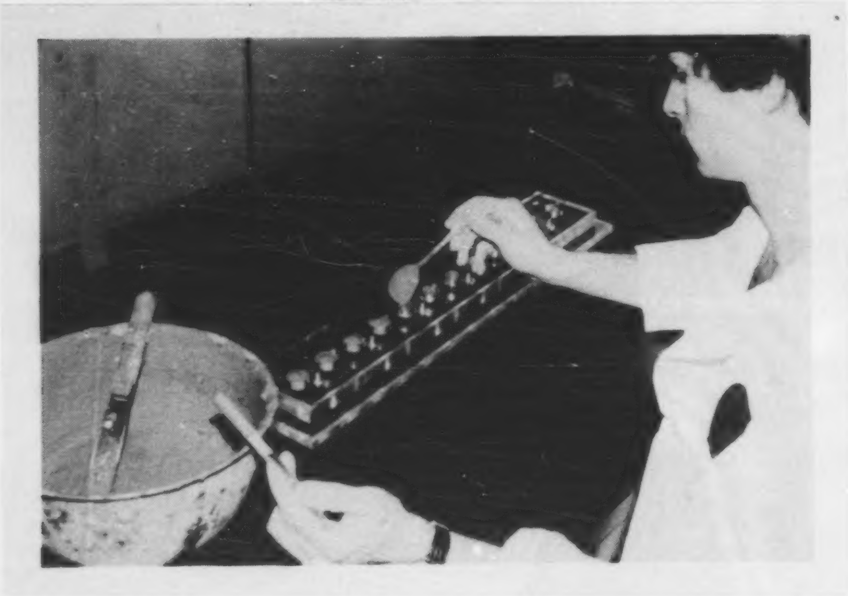

Figure 6. Preparation of cement-bentonite reactivity samples by spooning the grout into the mold.

Figure 7. Immersion of reactivity samples in chemical baths beneath an exhaust hood.

Figure 8. Reactivity samples in labelled, covered chemical baths within an exhaust hood.

which is a laboratory film produced by American Can Company. While this film was very resistant to chemical attack, it did not adhere to the beakers. Periodic observation of the samples was required to maintain the cover.

PERMEAMETERS

Background

The objectives of the permeability tests in this project were to determine the permeability of grouted soil samples to deionized water, and to measure the changes of their permeability due to long-term exposure to various chemicals. To run a permeability test on a grouted soil sample, two devices were needed:

1) a permeameter to encase the sample and confine the flow of the permeant, and
2) a permeability test apparatus to provide for the channeling of the permeants into and out of the permeameter with elevated head or permeant and allow the accurate measurement of flow through the sample

Permeameter Designs

- Rigid-Wall Permeameters

Several different permeameters were designed and tried. One of the initially promising designs used a rigid-wall cylindrical mold to serve as the grouting cylinder and then to confine both the sample and the permeant flow. The rigid-wall type permeameter was abandoned because of separation between the mold and the shrinking sample and a consequent short-circuiting of permeant flow. In addition, it was felt that the rigid-wall permeameter could affect permeability results if the grouted sample would have a tendency to swell as a reaction to the permeant.

- Original Triaxial Flexible-Wall Permeameter

Another early version of the permeameter was of a triaxial flexible-wall design. In essence, the grouted sample was encased in a flexible membrane consisting of a Teflon tape and a latex membrane, then placed and pressurized in a confining chamber filled with glycerine. Glycerine was used because it is more viscous than water and thus less likely to leak into the fittings (this leakage was a major problem to be overcome in Phase I). Permeant was introduced to the top of the sample at a desired pressure but lower than the confining pressure. An even lower backpressure could be applied to the tail end of the sample which helped reduce the volume of any gases trapped in the sample and thereby yield more accurate permeability values. The permeant that passed through the sample was collected at the bottom and measured for permeability calculations. Note that the confining pressure applied to the flexible membrane prevents the short-circuiting of the permeant along the sides of the grouted sample.

Specifically, the sample was placed between two porous stones, then between two 76.2 mm (3 in.) diameter aluminum (or an appropriate material) disks (base and cap) approximately 50.8 mm (2 in.) thick. This "sandwich" column was wrapped with Teflon tape to prevent the chemicals permeating through the sample from attacking the latex membrane surrounding the sample. Additionally, the tape and disk sides were smeared with high vacuum grease to control any small leaks. Next, a 0.64 mm (0.025 in.) thick latex membrane was unrolled over the surface of the column. Two 70 mm (2.75 in.) inside diameter o-rings were positioned over the membrane at each end, effectively squeezing the membrane into close contact with the greased disks. The combination of the high vacuum grease and the o-rings created an effective seal between the disks and membrane thus preventing the glycerine from leaking into the sample.

The sample was then placed in the confining chamber. This chamber was typically made of 9.5 mm (0.375 in.) thick clear acrylic tube, with an inside diameter of 108 mm (4.25 in.) and capped by two 19.1 mm (0.75 in.) thick aluminum endplates.

The base and cap disks, and thereby the sample, communicated to the outside of the confining chamber through 3.2 mm (0.125 in.) diameter nylon and brass fittings that passed through the endplates. Two 3.2 mm (0.125 in.) nylon tubes were attached to each disk--one, which was attached to the top disk, introduced leachate to the sample; the second was provided to bleed off any air trapped in the disk or the top porous stone (deairing will be discussed in a later section). This second line was closed by a valve during normal testing. One line to the bottom disk exited through the bottom endplate directly and carried off any permeant passing through the sample; the second line to the lower disk acted as a bleeder for the lower porous stone and disk. Both disks had a circular groove in their face to help disperse or collect fluid from a greater area of the porous stones (see Figure 9).

The permeameter design of Phase I called for the cap and base disks to be constructed of aluminum and the fittings to be made of brass. The cement in the cement-bentonite samples had a corrosive effect on the aluminum. For this reason several permeameters were constructed using brass for the base and cap disks. Permeameters were also constructed from Teflon and polyvinylchloride (PVC), using nylon fittings instead of brass. Furthermore some fittings were made of Monel and others of stainless steel allowing for a wider variety of chemicals to be tested.

The original permeameter had a total of twenty-four connection points (a connection point is a place of discontinued tubing). Two basic types of connections were used, one was a tapered pipe connection and the other a ferruled connection. The former was slightly more susceptible to leaks but was less sensitive to operator errors (e.g., ferrules not in proper place or direction).

- Modified Triaxial Flexible-Wall Permeameter

The original design was modified for several reasons. Some of the major considerations included:

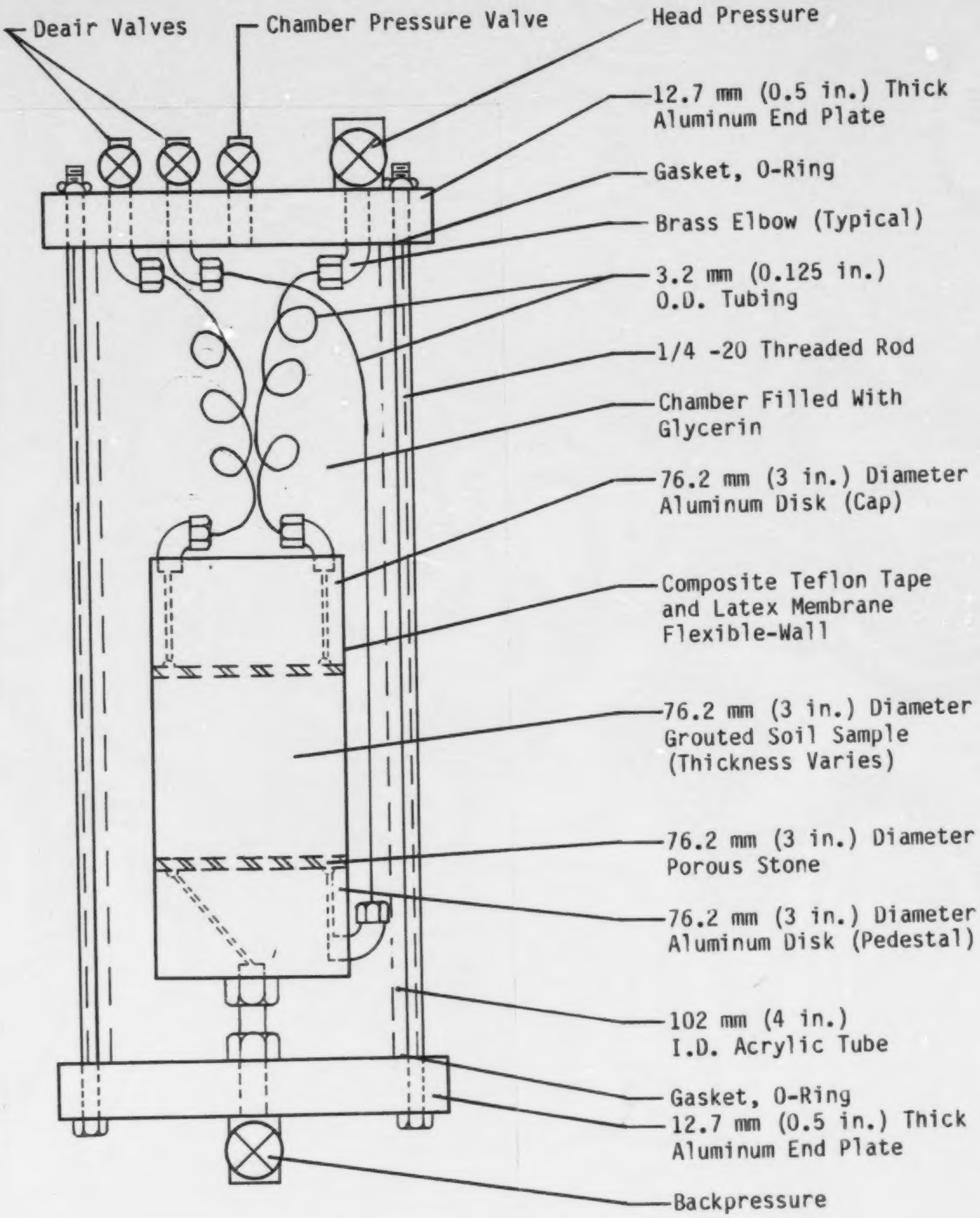
Deair Valves
Chamber Pressure Valve
Head Pressure
12.7 mm (0.5 in.) Thick Aluminum End Plate
Gasket, O-Ring
Brass Elbow (Typical)
3.2 mm (0.125 in.) O.D. Tubing
1/4 -20 Threaded Rod
Chamber Filled With Glycerin
76.2 mm (3 in.) Diameter Aluminum Disk (Cap)
Composite Teflon Tape and Latex Membrane Flexible-Wall
76.2 mm (3 in.) Diameter Grouted Soil Sample (Thickness Varies)
76.2 mm (3 in.) Diameter Porous Stone
76.2 mm (3 in.) Diameter Aluminum Disk (Pedestal)
102 mm (4 in.) I.D. Acrylic Tube
Gasket, O-Ring
12.7 mm (0.5 in.) Thick Aluminum End Plate
Backpressure

Figure 9. Details of the original triaxial flexible-wall permeameter.

1. Leaks developed occasionally, therefore, fewer connections were needed.
2. There was a lack of compatibility between the permeameter and some of the chemical permeants. In the original design, chemicals came into contact with the endplates.
3. General operation of the permeameter was awkward and manipulation of the connections was difficult.
4. It was desired to use higher pressure; a stronger permeameter was required to withstand the increased pressures.

The modified permeameter depicted in Figure 10 consisted of four 3.2 mm (0.125 in.) TUBE x 3.2 mm (0.125 in.) TUBE teflon-packed 316 stainless steel plug valves (two for deairing, one for headpressure and one for tailpressure; one 3.2 mm (0.125 in.) NPT brass body assembly quick-connect (for chamber pressure); one 3.2 mm (0.125 in.) NPT purge valve (for chamber venting); four 3.2 mm (0.125 in.) NPT x 3.2 mm (0.125 in.) TUBE brass male connectors; two 19.1 mm (0.75 in.) thick aluminum endplates; four 9.5 mm (0.375 in.) x 20 stainless steel rods; four 9.5 mm (0.375 in.) x 20 stainless steel wing nuts with washers; one 127 mm O.D. x 305 mm x 12.7 mm (5 in. O.D. x 12 in. x 0.5 in.) acrylic tube; two neoprene gaskets; 3.2 mm (0.125 in.) flexible nylon tubing; one 6.35 mm (0.25 in.) NPT x 63.5 mm (2.5 in.) stainless steel nipple; two 3.2 mm (0.125 in.) NPT x 3.2 mm (0.125 in.) TUBE nylon connectors; two 3.2 (0.125 in.) NPT x 3.2 mm (0.125 in.) TUBE nylon elbows; two 76.2 mm DIA x 50.8 mm disks (3 in. DIA x 2 in.) which were made of various materials and were interchangeable, one serving as a pedestal and the other as a cap; two 76.2 mm DIA x 6.35 mm (3 in. DIA x 0.25 in.) porous stones; and four 76.2 mm (3 in.) O.D. rubber o-rings.

The modified permeameter was much more hassle-free than its predecessor. Leaks were not as great a concern due in part to a third less connection points (only sixteen total) and partially because there was a higher percentage of ferruled connections as opposed to tapered connections (tapered connections are more susceptible to leaks). The modified permeameter had only four tapered connections with the remaining twelve being ferruled connections.

Item 2 listed above relates to the compatibility of the permeameters with the chemical leachate and/or grouted soil itself. The modified design utilized a continuous piece of 3.2 mm (0.125 in.) flexible nylon tubing which extended from the four stainless steel control valves to the 76.2 mm (3 in.) DIA pedestal and cap. Prior to this change the chemical permeant came into contact with the endplates. Table 3 was used to determine the appropriate equipment mix that would perform satisfactorily when subjected to any of the listed chemical leachates. In the original permeameter, endplates, caps and pedestals had to be interchanged depending on the chemical used. The modified permeameters were constructed of 316 stainless steel and nylon fittings because these materials were compatible with most of the chemical leachates studied. Therefore, only the pedestal and the cap needed to be interchangeable. They were designed to facilitate a quick and effortless replacement.

Item 3 above pertains to the preparation of the sample in the permeameter and general operation of the permeameter itself. In comparison to the original permeameter, the overall preparation of the sample in the modified permeameter

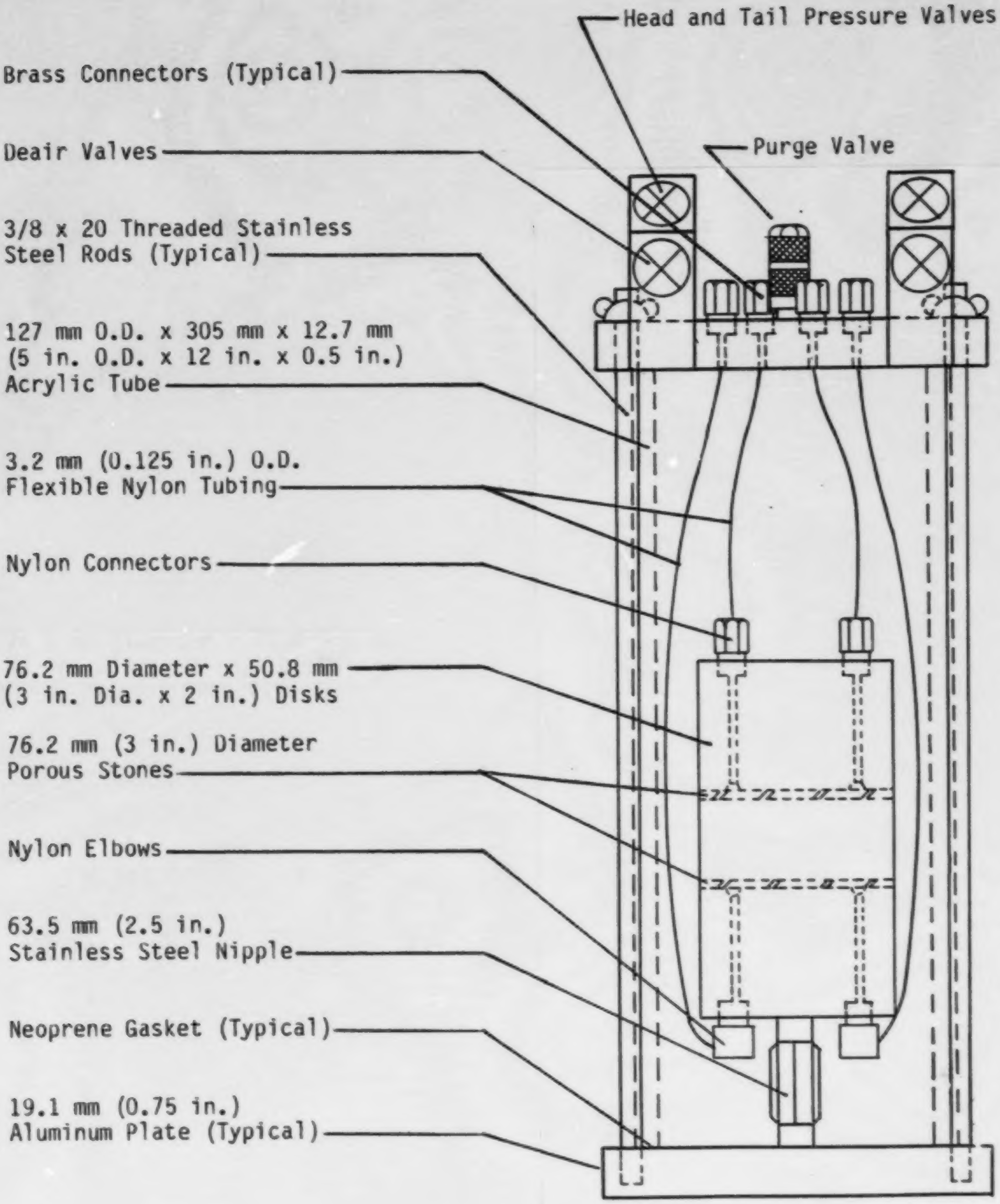
Head and Tail Pressure Valves
Brass Connectors (Typical)
Deair Valves
Purge Valve
3/8 x 20 Threaded Stainless Steel Rods (Typical)
127 mm O.D. x 305 mm x 12.7 mm (5 in. O.D. x 12 in. x 0.5 in.) Acrylic Tube
3.2 mm (0.125 in.) O.D. Flexible Nylon Tubing
Nylon Connectors
76.2 mm Diameter x 50.8 mm (3 in. Dia. x 2 in.) Disks
76.2 mm (3 in.) Diameter Porous Stones
Nylon Elbows
63.5 mm (2.5 in.) Stainless Steel Nipple
Neoprene Gasket (Typical)
19.1 mm (0.75 in.) Aluminum Plate (Typical)

Figure 10. Details of the modified triaxial flexible-wall permeameter.

expended less time and energy. The modified permeameter appeared to be less susceptible to line crimping. The position of the tail pressure valve in the original permeameter did not lend itself well to ease of operation. It was very awkward to operate plus it was rather difficult to make the appropriate connections. In addition, the brass needle shutoff valves (deair valves) were not easily operated in comparison to the plug valves equipped on the modified permeameter.

In summary, both permeameter designs worked satisfactorily but the modified design yielded fewer operating problems, was more time efficient to use, and operated more easily.

Procedure for Mounting Grouted Soil Samples

The recommended procedure for mounting grouted soil samples may be outlined as follows:

1. Carefully clean and deair porous stones in boiling water
2. Properly attach selected pedestal to base endplate
3. Position two o-rings under and around the pedestal
4. Carefully position a rolled-up latex membrane around the pedestal, placing it towards the bottom edge
5. Sandwich a clean porous stone, grouted soil sample, and another clean porous stone in between the pedestal and cap (steps 1-5 are shown in Figure 11)
6. Apply teflon tape (the first layer of the composite flexible membrane)
    a. Use tape that is 50 mm (2 in.) wide. Roll off 300 mm (12 in.) length, holding each end between thumb and forefinger with adhesive facing operator. Keep the tape taut at all times.
    b. Wrap the tape tightly around the grouted sample--15 mm (0.5 in.) minimum should adhere to the pedestal (see Figure 12). Co-worker may have to apply pressure to top cap to prevent movement of the cylindrical assembly. Check the following:
        i. ends of tape should be overlapped approximately 30 to 40 mm (1.0 to 1.5 in.) with no "dog-ears" underneath the overlap
        ii. no wrinkles in the tape, especially in the vertical direction
        iii. good adhesion to pedestal
        iv. no holes in tape
    c. Apply second layer of tape if needed (depends on thickness of sample), see d through f below if extra layers of tape are needed
    d. Roll off another 300 mm (12 in.) length, holding each end between thumb and forefinger with adhesive facing operator. Keep tape taut at all times.
    e. Apply second layer of tape so that its end-overlap is opposite the first layer overlap
    f. Wrap tape tightly around the grouted sample-15 mm (0.5 in.) minimum should adhere to the cap with remaining tape overlapping the first tape layer (again 15 mm (0.5 in.) minimum for edge overlap of tape layers--may need three layers of tape to cover entire grouted sample). Co-worker may have to apply pressure to cap in order to prevent movement of assembly. Check for the following:

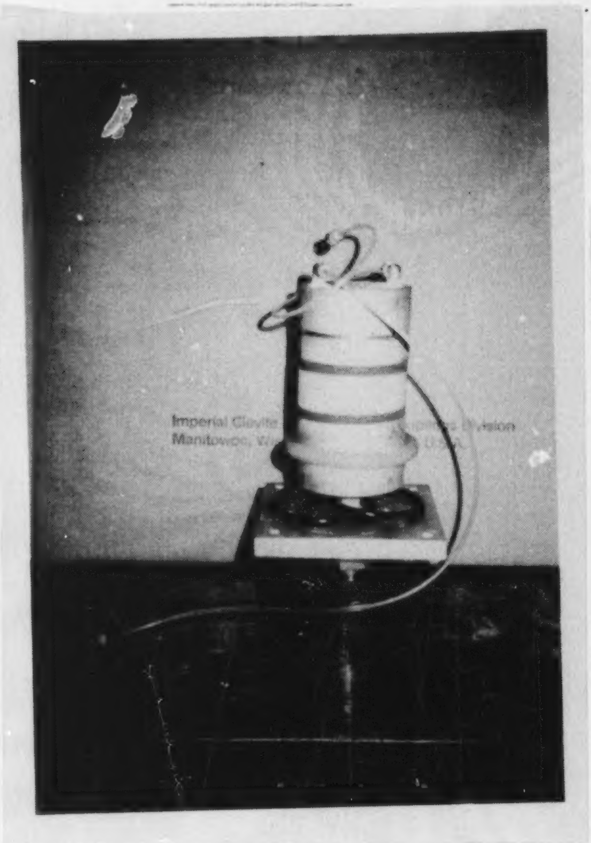
Imperial Clevite
Manitowoc, W

Figure 11. General arrangement of materials as a grouted soil specimen is mounted in the permeameter.

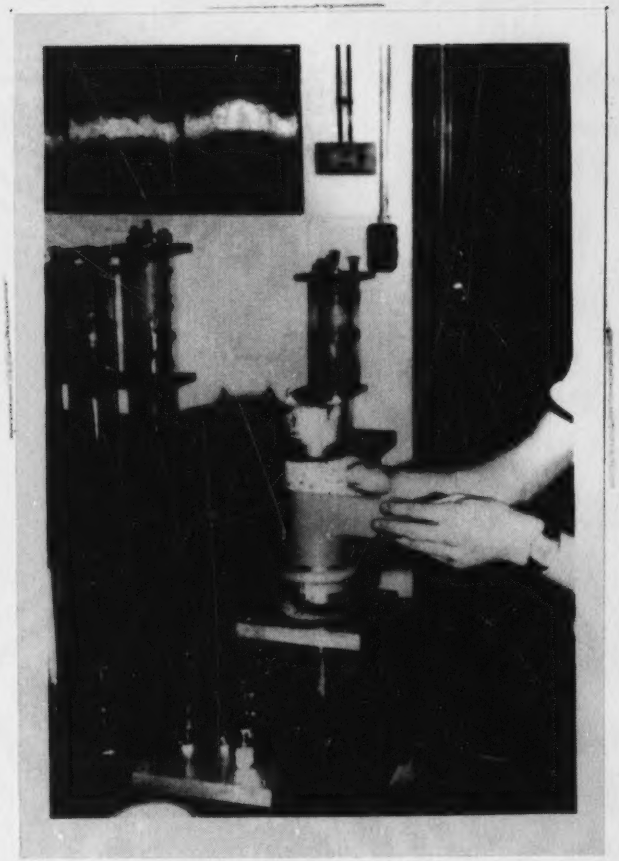

Figure 12. Application of teflon tape to a mounted soil specimen.

    i. ends of tape should be overlapped approximately 30 to 40 mm (1.0 to 1.5 in.) with no "dog-ears" underneath the overlap
    ii. no wrinkles in tape, especially in the vertical direction
    iii. good adhesion to cap
    iv. no holes in tape
7. Smear a thin layer of vacuum grease cylindrically around the entire length of the pedestal through cap assembly
8. Carefully unroll the latex membrane (the second layer of the composite flexible membrane) upwards toward cap (see Figures 13 and 14)
9. Stretch two 76.2 mm (3 in.) O.D. o-rings around the pedestal and two around the cap. The key is to build up a "ring" of grease when o-rings are pulled into place (this provides assurance against developing chamber fluid leaks into the grouted soil sample; see Figure 15)
10. Cut four lengths of 3.2 mm (0.125 in.) flexible nylon tubing (two @ 500 mm (20 in.) and two @ 400 mm (16 in.). Attach 500 mm (20 in.) lengths to the nylon elbows positioned on the pedestal and 400 mm (16 in.) lengths to the connectors positioned on the cap. Tighten fittings appropriately.
11. Place 127 mm (5 in.) O.D. acrylic tube around the cylindrical assembly making sure the gaskets are in proper place and that the 3.2 mm (0.125 in.) tubing is "fished" to the top of the acrylic tube without crimping the tubing.
12. Feed the four lengths of 3.2 mm (0.125 in.) tubing through the couplers in the top endplate; pull lines through so top endplate freely rests on the acrylic tube.
13. Place the four 9.5 mm (0.375 in.) x 20 stainless steel threaded rods into place. Tighten rods to bottom endplate. Proceed by putting a stainless steel washer and nut on ends of the threaded rods that protrude through the top endplate. Tighten appropriately making sure that gaskets and the acrylic tube are aligned properly.
14. Attach the four continuous lengths of tubing to their proper 316 stainless steel plug valves. Two lines coming from the pedestal should be connected to the valves on the left and the two lines from the cap to the valves on the right (see Figure 16). Note: attach 3.2 mm (0.125 in.) tubing to the ferruled fittings that are facing the "inside". Tighten fittings appropriately.
15. Tighten connectors one quarter turn past snug by finger pressure.
16. Fill chamber with glycerin
    a. Open purge valve on top endplate
    b. Insert quick-connect from glycerin pressurized reservoir
    c. Fill the chamber with glycerin until all the air is displaced by the chamber fluid
    d. Close purge valve
    e. Disconnect quick-connect
17. Permeameter with grouted soil sample is ready for testing (see Figure 16).

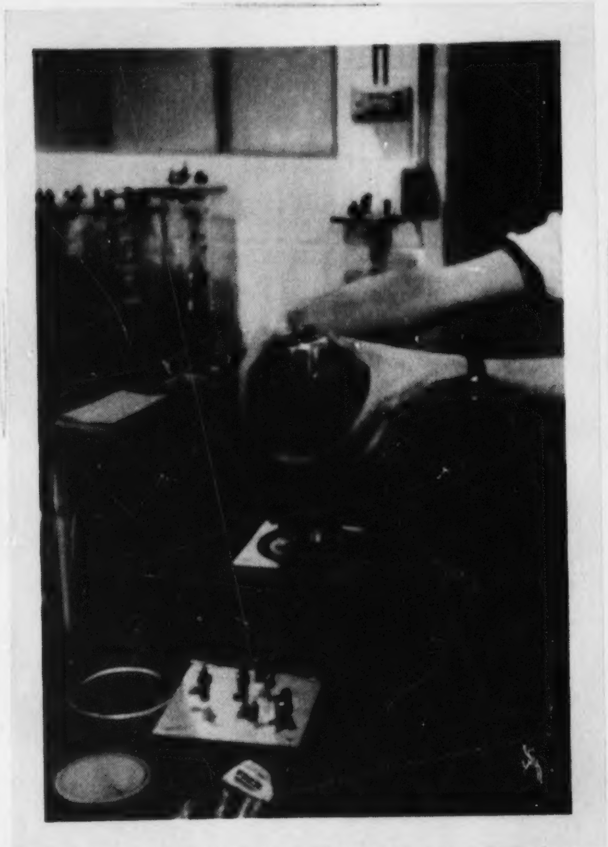

Figure 13. Unrolling of a latex membrane over a grouted soil specimen.

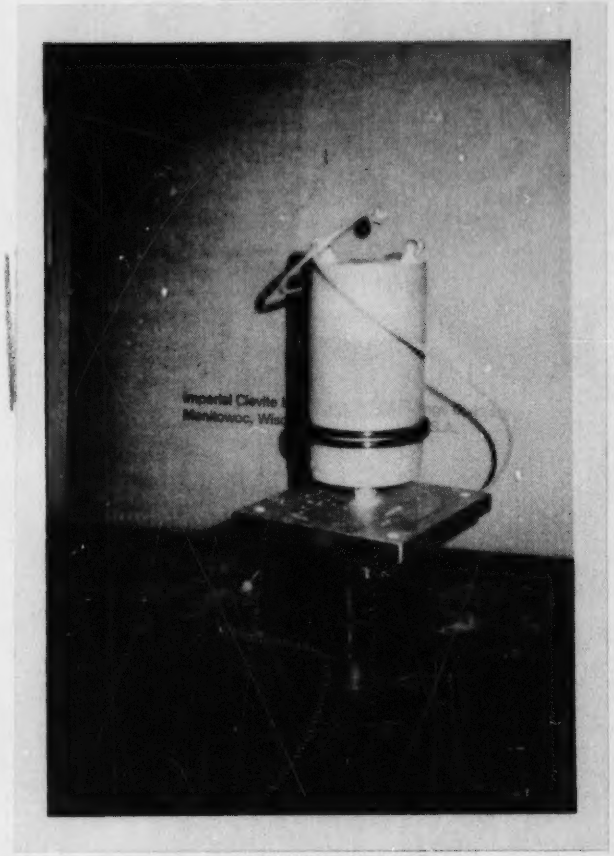
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Figure 14. Composite teflon tape-latex membrane flexible-wall assembly for a grouted soil specimen.

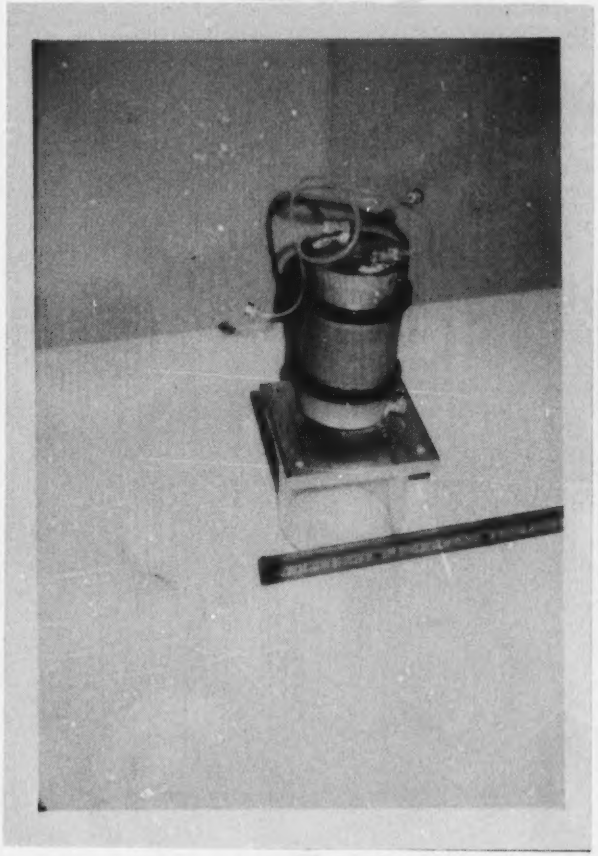


Figure 15. Grouted soil sample assembly completed and readied for piping connections.

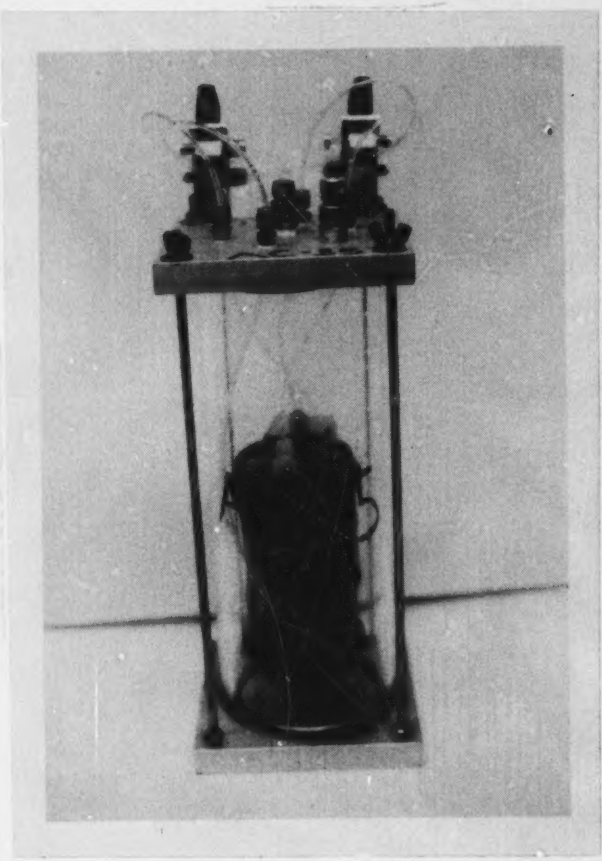


Figure 16. Completely assembled sample in a modified triaxial flexible-wall permeameter.

PERMEABILITY MEASURING APPARATUSES AND TESTING METHODS

Environmental Boxes and Testing Boards

Percolation of the leachate through the grouted soil sample was performed in one of three testing apparatuses. Each of the three permeation devices was constructed based on the modified falling-head principle. One method utilized testing boards (or boards hereafter). The other two permeability apparatuses, designated as environmental glove box A and environmental glove box B, were vented boxes utilizing a one pass air system to remove hazardous vapors. They were constructed of 12.7 mm (0.5 in.) thick acrylic plexiglass.

- Environmental Glove Box A

Environmental glove Box A (reference Figure 17) was a second-generation (phase III) box used primarily for the permeation of chemical leachate. It was a 0.91 m x 1.22 m x 2.44 m (3.0 ft. x 4.0 ft. x 8.0 ft) enclosure made of 12.7 mm (0.5 in.) clear plate acrylic plexiglass. The glove box was composed of three subcompartments, namely, permeation, reservoir, and control compartments. The permeation compartment encompassed roughly half of the entire space. The remaining space was split between the reservoir and control compartments.

The permeation compartment housed the permeameters during the percolation process and could be accessed through one of two end-wall doors or by way of a door and two portholes located on each side. Maximum capacity was twenty triaxial type permeameters. Clear flexible polyvinyl tubing (6.35 mm, 0.25 in.) transported regulated air to the chamber fluid of the permeameters while 3.2 mm (0.125 in.) nylon tubing carried leachate from the pressurized reservoir to the permeameter and then on to the standpipes following permeation.

The reservoir compartment had two shelves, a lower shelf containing the pressurized reservoirs and an upper shelf upon which the refill bottles were stored. It could be entered by use of an access door towards the rear of the box or by way of two gloved-portholes. The lower shelf could hold a maximum of ten pressurized reservoirs at any given time. These reservoirs supplied the leachate directly to the permeameters. The reservoirs themselves were periodically resupplied, via gravity through 6.35 mm (0.25 in.) clear flexible nylon tubing, with leachate from refill bottles stored on the upper shelf. In addition, the pressurized reservoirs required regulated air which was channeled through 6.35 mm (0.25 in.) polyvinyl tubing from the control compartment, the origin of all air pressure regulators, gauges, and standpipes (flow measuring burets).

In the control compartment, entrance could be made by way of two small access doors and/or through two portholes at the front of the box. Entrance was required only to reset the standpipes or to adjust one of two main air pressure sources, one for the control of the chamber pressure, and another for driving head pressure. As arranged through a series of gauges/regulators, four different chamber pressures could be applied at any time. Each regulator/gauge was connected to six header outlet ports, thus providing a total of

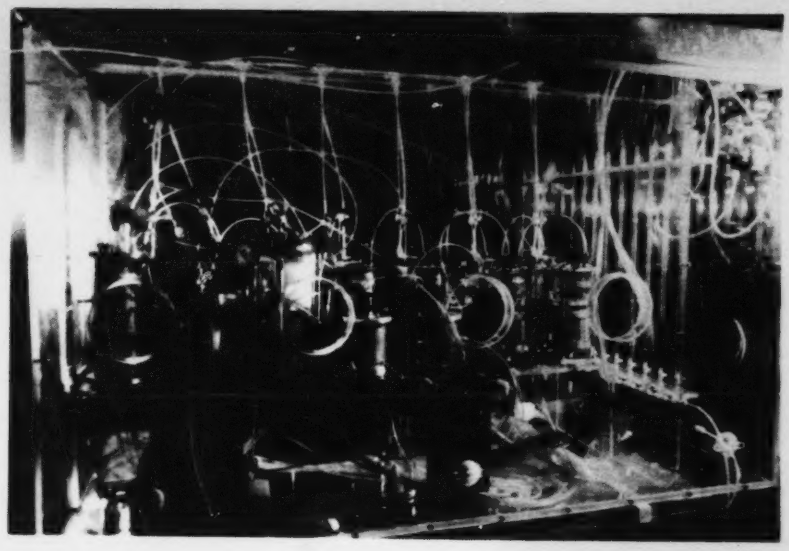


Figure 17. A view of environmental glove box A showing (from left to right) the permeant reservoirs, permeameters, and the buret banks.

twenty-four ports (a maximum of twenty ports were in use at any time). Chamber pressure refers to the pressure which was exerted on the grouted soil sample via the chamber fluid. This pressure, coupled with driving headpressure and a backpressure equal to zero (buret vented to the atmosphere), allowed for the calculation of net confining pressure (effective stress), gradient, and most importantly, permeability.

Four different driving headpressures could also be applied at any one time. These pressures were controlled from a panel that was equipped with four regulators which were connected in parallel to one pressure gauge. Each regulator in turn supplied a header of four outlet ports, thus providing a total of sixteen ports (a maximum of ten were utilized at any given time). It is appropriate to note here that the driving headpressure was the direct air supply source feeding the pressurized reservoirs. Driving headpressure refers to the pressure which was exerted on the leachate in order to establish a flow potential (gradient), a prerequisite for the flow of any fluid.

One additional component essential in the control compartment was the standpipe (standard buret). Each of the twenty stations in environmental glove box A had a 50 cc buret to measure the leachate that had percolated through the grouted sample. Flasks were attached via 3.2 mm (0.125 in.) nylon tubing to five burets each, in order to circumvent overflow spills due to loss of permeability integrity of the samples. To reset the standpipe one would execute the following standard procedure:

1. Record the standpipe fluid level (read bottom of fluid meniscus)
2. Record time when standpipe reading was taken
3. Drain leachate to appropriate level by opening standpipe valve
4. Let approximately two minutes elapse
5. Check fluid level in pressurized reservoir, refill as needed
6. Record the standpipe fluid level (read bottom of meniscus)
7. Record time when standpipe reading was taken
8. Check chamber and driving headpressures, readjust accordingly

The effluent from the burets was channeled via gravity through 6.35 mm (0.25 in.) nylon tubing to hazardous waste containment bottles located beneath the central glove box. The containment bottles were safely protected at floor level by plywood enclosures. Each bottle was sealed with an airtight cap that was fitted with two connectors. One connector transported effluent while the other was used to vent harmful vapors into the permeation compartment where they were removed by the one pass air system.

Several advantages resulted from this particular glove box design. First, the need for a large number of gradient and net confining pressure combinations could be met. Second, very small permeabilities, 1.0×10^{-11} cm/sec, could be accurately measured. Third, the potential of developing leaks in the system was rather small. Fourth, the design allowed for twice as many permeation stations as compared to glove box B which was of comparable size. Fifth, no permeation stations were connected to a common pressure source, thus allowing for greater flexibility in relation to effective stress/gradient combinations, although a finite number of different combinations existed. Finally, the overall design provided the operator a safe working environment. In contrast there were a couple of disadvantages. First, only a backpressure of zero could exist. Second, the system was not capable of measuring influent, only effluent. Hence, system leaks had the potential of being hard to detect (although, as previously pointed out, the potential for leaks was quite small). Lastly, the amount of gas formation could not be measured.

- Environmental Glove Box B

Environmental glove box B, like box A, was used primarily for the permeation of chemical leachate. This first-generation (Phase II) apparatus ensured the safe removal of toxic vapors. However, unlike box A, it was not subdivided into three compartments. Glove box B had a tubing and valve layout which was identical to the testing boards, hence box B was oriented by station rather than by function. Therefore, the resetting operation of the permeation stations was identical to that of the testing boards (discussed in the next section) except for the containment and handling of the permeant. The refill reservoirs did not operate by gravity; they needed to be pressurized to a maximum of 34.5 kN/m^2 (5 psi). The effluent had to be contained and properly vented to ensure safe removal of harmful fumes. The flow from permeation station to effluent bottle was via gravity. The bottles were safely protected at floor level by plywood enclosures. Each bottle was sealed with an airtight cap that was fitted with two connectors, one for effluent flow and the other to vent harmful vapors into the confines of the glove box where they could be safely removed by the one pass air system.

Glove box B was a 0.91 m x 1.22 m x 2.44 m (3 ft. x 4 ft. x 8 ft.) box made of 12.7 mm (0.5 in.) thick acrylic plexiglass with access doors at both ends (see Figure 18). It had a capacity of ten permeameters (ten permeation stations). Each two stations shared a chamber, driving head, and tailpressure (backpressure) regulator/gauge system. Thus, stations 1 and 2, 3 and 4, 5 and 6, 7 and 8, 9 and 10 shared the regulator/gauges in series. From this vantage point the system offered moderate flexibility. Six of the stations were equipped with brass and nylon hardware. Of the remaining four stations, two incorporated 316 stainless steel fittings and valves, and two contained Monel fittings and valves. All brass and stainless valves were teflon packed plug valves, thus eliminating erroneous standpipe levels which could potentially occur by the closing and opening operation of the valves. Most of the tubing throughout the box consisted of Imperial Eastman semi-rigid 6.35 mm (0.25 in.) O.D. clear flexible nylon tubing except for the 12.7 mm (0.5 in.) O.D. nylon standpipes which could be switched on during the percolation process of larger leachate flow. Glove box B had basically the same advantages and disadvantages as the testing boards (discussed in the next section). An additional advantage was that it minimized, in several ways, direct operator contact with the cylinder once the permeameter was placed within the glove box, including:

1) All permeameters and refill reservoirs were contained within the confines of the plexiglass box.
2) All connections and other manipulations of the cylinder and reservoirs were performed via the use of neoprene gloves that were attached to eight (four per side) evenly spaced portholes running the length of the box.

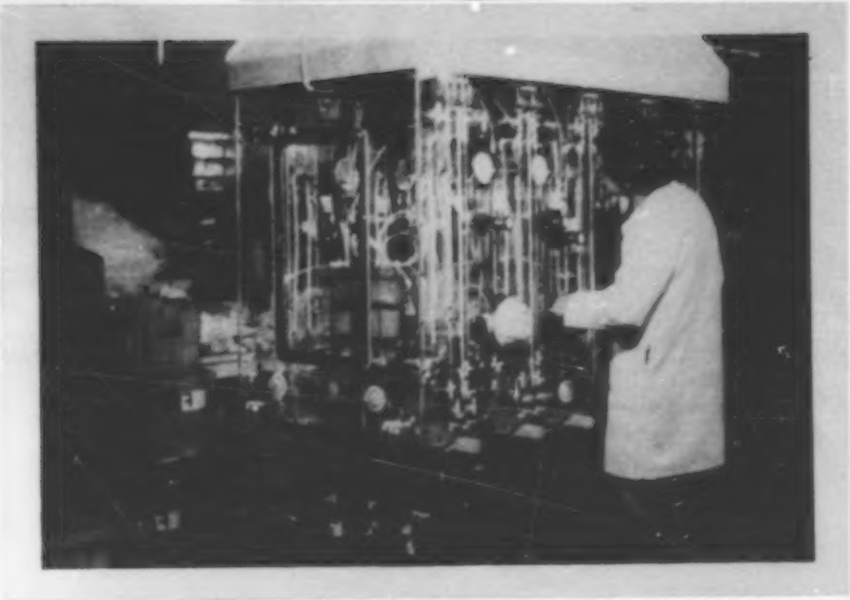


Figure 18. Environmental glove box B, used primarily for the percolation of chemical leachate, in full operation.

3) Handles of the regulators and valves protruded through the box and could be operated entirely from outside.
4) The environmental glove box was connected to a one pass air system which continuously removed hazardous vapors from within.

- Testing Boards

The testing board, another type of testing apparatus, was used principally when water was the permeant (all test cylinders were first permeated with deionized water to establish a baseline permeability). The boards were also used in Phases I and II for the permeation of samples with acetone and ethylene glycol. The boards consisted of a relatively simple design (see Figure 19). Referencing Figure 20, the schematic drawing, the flow path is shown for the two-standpipe system (headpipe and tailpipe). Resetting of the testing board (also environmental glove box B) consisted of the following procedure:

1. Record the headpipe and tailpipe fluid levels (read bottom of meniscus)
2. Record time when standpipe readings were taken
3. Close both headpipe and tailpipe pressure valves (1 & 2) and valves Y and Z on the permeameter; see Figure 20
4. Open both headpipe and tailpipe vent valves (3 & 4)
5. Refill headpipe to appropriate level by operating feed valve (5). [In addition, for glove box B the refill reservoir will have to be pressurized. Apply no more than 34.5 kN/m^2 (5 psi) to reservoir-regulator/gauge at end of box.]
6. Drain tailpipe to appropriate level by operating drain valve (7)
7. Close both headpipe and tailpipe vent valves (3 & 4), observe relative fluid level
8. Open both headpipe and tailpipe pressure valves (1 & 2), then open valves Y and Z on the permeameter
9. Allow two minutes to elapse
10. Record the headpipe and tailpipe fluid levels (read bottom of meniscus)
11. Record time when standpipe readings were taken
12. Check chamber, driving head, and tailpressures (backpressure); readjust as needed.

Channelization of the leachate was via 6.35 mm (0.25 in.) clear flexible nylon or polyvinyl tubing. All fittings consisted of either brass or nylon. Specifically, fittings such as tees, elbows, and straight connectors were composed of nylon. Valves were constructed of brass and had o-rings of various composition. Plug type valves were used to eliminate erroneous standpipe readings due to the closing and opening operation. Typically there were three permeation stations per testing board. Each board had a set of three gauges and regulators. One gauge was needed to pressurize the chamber of the triaxial (flexible-wall) permeameters. The other two were utilized to maintain specified gradients. One operated the driving headpressure and the other controlled the tailpressure (or backpressure).

There were several advantages to this particular design, including:

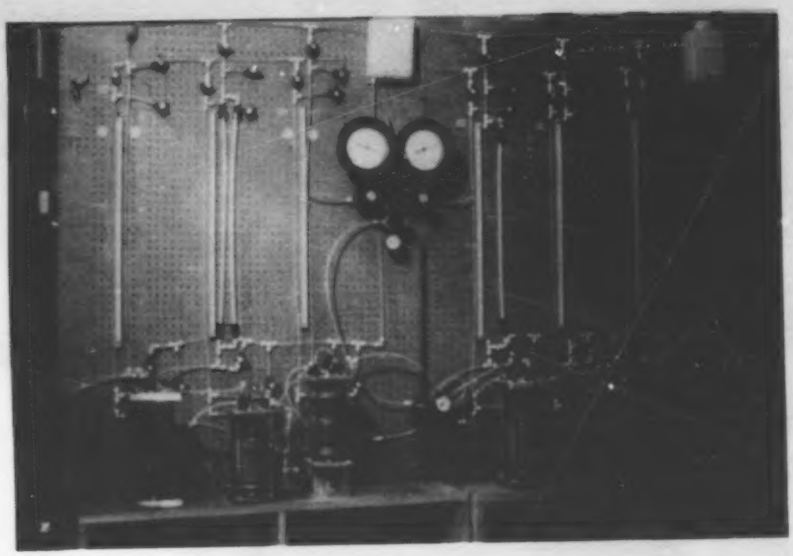


Figure 19. Typical testing boards setup for initial permeation of the grouted samples with deionized water to establish a baseline permeability

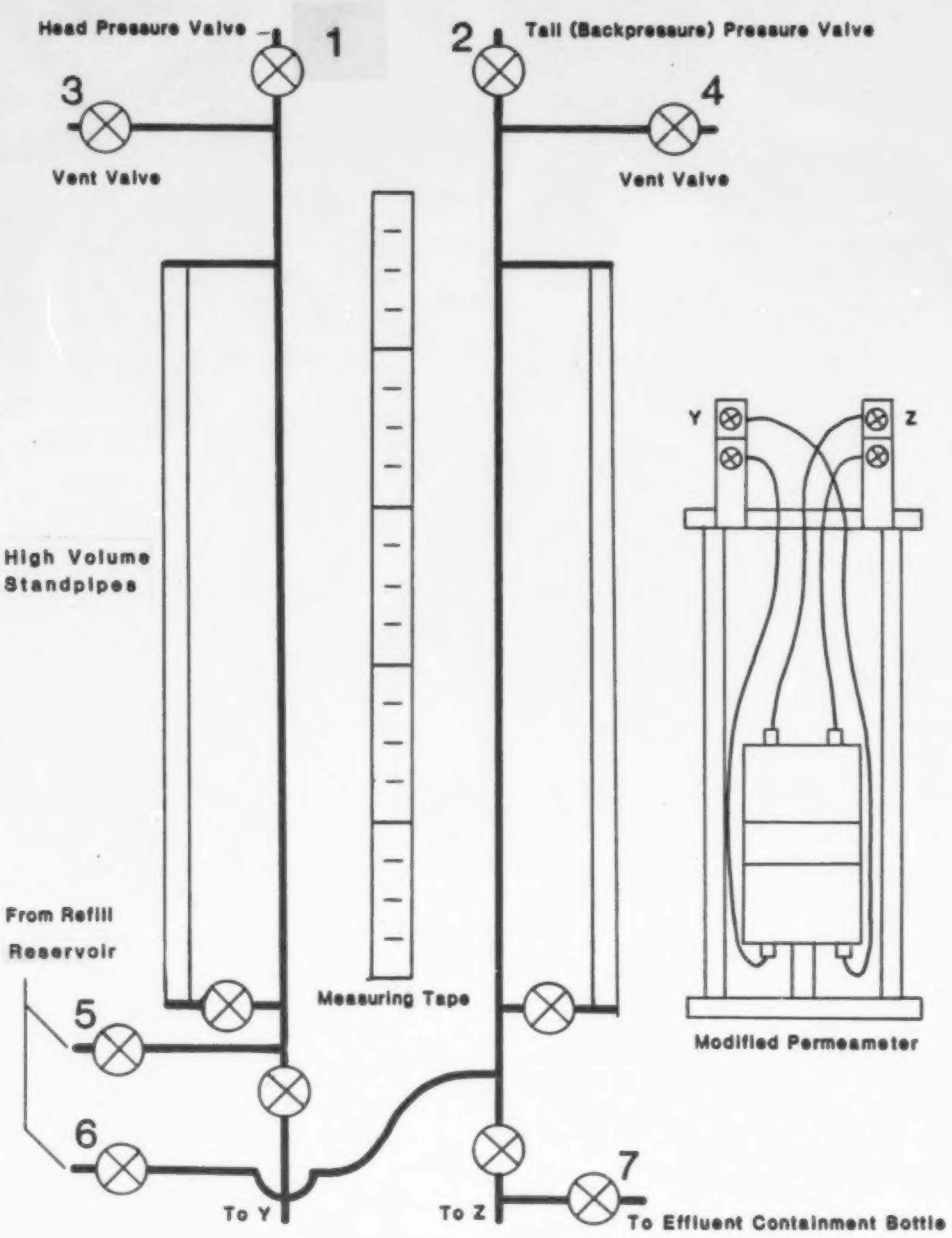

Head Pressure Valve
1
2
Tail (Backpressure) Pressure Valve
3
4
Vent Valve
Vent Valve
High Volume
Standpipes
Y
Z
From Refill
Reservoir
5
Measuring Tape
Modified Permeameter
6
7
To Y
To Z
To Effluent Containment Bottle

Figure 20. Schematic drawing of testing boards system showing the station with high volume standpipes.

1. Various gradient and net confining pressure (effective stress) combinations were possible
2. The backpressure could be controlled at a desired level
3. The system monitored influent and effluent, thus giving important checks on (a) the development of system leaks, and (b) gas production caused by grout/leachate reaction
4. The relative amount of air in the system (influent and effluent tubing and permeameter) could be monitored (if air is present in the system, releasing either the driving headpressure or backpressure will yield an increase in standpipe fluid height)
5. Very small permeabilities (as low as 1.0×10^{-11} cm/sec) could be measured accurately

The testing board design was not without pitfalls. One was that the system had many connections due to the valves that were required to obtain the advantages cited previously. Hence, the potential for developing leaks was quite high. A second disadvantage was that three permeability stations were connected in series, thus hindering the flexibility of the chamber, driving head, and backpressure settings.

Permeability Testing and Its Procedure

Permeability is, by far, the most variable soil property known to geotechnical engineers. Permeability is the ability of a fluid to flow through a porous medium, the porous medium being a grouted soil for this research. In order to have fluid flow there first must exist a potential energy differential between two specified points. Based on fluid mechanics, the hydraulic gradient is the potential energy dissipated in driving the liquid through the soil. The hydraulic gradient is defined as the slope of the piezometric heads between two points in confined flow (i.e., head loss, Δh, that occurs across the length, L, of a soil sample; hydraulic gradient (i) = $\Delta h/L$). To further develop a relationship between hydraulic gradient and permeability, one must incorporate the use of the continuity equation, $Q = vA$; and Darcy's law, $v = ki$, where:

Q = volume of flow per unit time, (L^3/t)
A = cross sectional area of flow channel (L^2)
v = velocity of flow, (L/t)
k = permeability, (L/t)
i = hydraulic gradient, (L/L)

Through the manipulation of these equations a general relationship can be established:

$$k = Q/(iAt)$$

This can be specially tailored to various permeability test conditions. The authors' specific research utilized a modified falling-head permeability test. The following equation was adapted for all permeability calculations:

$$k = \frac{al}{At} \ln \left[\frac{h_1}{h_2} \right]$$

where:

a = cross sectional area of standpipe, (L^2)
t = time
h_1 = initial height of permeant in standpipe (plus pressure head in feet) at time zero, (L)
h_2 = height of permeant in standpipe (plus pressure head in feet) after elapsed time of t, (L)
l = length of sample (flow path, L)
A = cross sectional area of the sample, (L^2)
$\ln$ = logarithm to base 2.7182818...

Many parameters could potentially affect the permeability of grouted soil samples, such as (1) various grouted soil characteristics, for example, grain size, void size, degree of interconnectedness of voids, packing of soil grains, amount of entrapped air (degree of saturation), and grout content per volume of soil; (2) type of grout; (3) type of leachate and its characteristics such as viscosity, concentration, molecular make-up; (4) reaction between leachate and grout; (5) gradient; and (6) net confining pressure.

All the above mentioned parameters, except #4, can be controlled to a great extent by careful observance of established testing procedures. Such procedures have been previously explained in this report in detail, for example the grouting of soils, mounting of the grouted sample into the triaxial permeameter, and the actual process of permeability testing as described in the following paragraphs.

Permeability testing can be subdivided into four categories: (1) initial start up, and deairing of the permeameter; (2) permeation with water; (3) permeation with chemical leachate; and (4) dismantling of the permeameter after testing is complete. These four categories are discussed in the following sections.

◦ Initial Start Up and Deairing

Initial start up and deairing of the permeameter is important for a number of reasons, including (1) consolidation of the sample at the desired net confining pressure (effective stress); (2) to check the permeation station and permeameter for leaks; and (3) to remove unwanted air from the system that could potentially infiltrate the grouted soil sample and artificially reduce its permeability. The procedure for initial start up and deairing of the permeameter is given below assuming one was using the testing boards (reference Figure 19 and 20). The deairing procedure for environmental glove boxes A and B was similar. The procedure consisted of the following steps:

A. Connect permeameter to chamber pressure
    1. Vent headpressure, tailpressure (backpressure), and both bleeder valves (1, 2, 3, and 4 as shown in Figure 20)
    2. Connect chamber pressure lines to the permeameter
    3. Adjust chamber pressure to achieve desired net confining pressure (effective stress)
    4. Let the permeameter sit for approximately 24 hours

5. Test for leaks
    a. deair head and tail lines at 41.5 to 55.0 kN/m^2 (6 to 8 psi)
        i. close both pressure valves (1 and 2) and both bleeder valves (3 and 4); connect one at a time to deionized water supply (standpipe)
        ii. open pressure valve (1 or 2)
        iii. open bleeder valve (3 or 4)
        iv. periodically (at 15 second intervals) close bleeder valve (3 or 4)
        v. continue processes (iii) and (iv) until air has been purged from lines
        vi. close bleeder valve (3 or 4)
        vii. close pressure valve (1 or 2)
    b. fill standpipes to appropriate levels (half fill standpipe)
    c. vent both head and tail standpipes (3 and 4)
    d. monitor fluid level for 24 hours

B. Connect permeameter to vacuum (stages 1 and 2)
  1. Connect head line to vacuum for 24 hours (stage 1)
    a. connect vacuum source to head bleeder valve on permeameter
    b. close head vent valve (3)
    c. vent tail standpipe (this is the source of leachate to be measured)
    d. adjust chamber pressure to achieve desired net confining pressure
    e. open head bleeder valve
    f. take readings on head and tail standpipes
    g. let test run for 24 hours
    h. take readings on head and tail standpipes
  2. While vacuum is still connected to head bleeder valve and valve is still open:
    a. open head feed valve (5)
    b. periodically (at 15 second intervals) close bleeder valve
    c. continue processes (a) and (b) until air has been purged from head line
    d. close bleeder valve
    e. close head feed and vent valves
    f. disconnect vacuum supply from head bleeder valve
  3. Connect tail line to vacuum for approximately one week (stage 2)
    a. connect vacuum source to tail bleeder valve on permeameter
    b. close tail vent valve (4)
    c. vent head standpipe (this is the source of leachate to be measured)
    d. adjust chamber pressure to achieve desired net confining pressure
    e. open tail bleeder valve
    f. take readings of tail and head flow standpipes
    g. take readings every day for one week

C. Apply "normal" pressures to head and tail line
  1. While vacuum is still connected to tail pressure valve:
    a. close tail pressure valve
    b. connect tail bleeder valve to a deionized water supply (standpipe)

   - c. open tail bleeder valve
   - d. periodically (at 15 second intervals) close bleeder valve
   - e. continue processes (c) and (d) until air has been purged from head line
   - f. close bleeder valve
   - g. close head and tail pressure valves
   - h. disconnect vacuum supply from tail pressure valve

2. Connect tail line (standpipe) to tail pressure valve
3. Adjust head and tail pressure to obtain desired net confining pressure and gradient
4. Fill head and tail standpipes to appropriate levels
5. Close head and tail line vent valves
6. Open head and tail line flow valves
7. Open head and tail pressure valves
8. Take readings at regularly scheduled times

∘ Permeation with Water

The main objective of this research study was to investigate the changes in permeability of grouted soil samples that were exposed to various chemical leachates (hazardous wastes). The first step towards obtaining this goal was to permeate all the grouted samples prior to chemical percolation with deionized water until an equilibrium baseline permeability was established. Equilibrium was assumed to be reached based upon two seemingly subjective criteria. First, the graph of permeability versus flow in pore volumes had to "level" out. Second, at least 0.5 to 1.0 pore volumes of water had to pass through the sample. During Phase II the confining pressure varied but during the percolation process of Phase III the net confining pressure for all grouted samples was maintained at 121 kN/m^2 (17.5 psi) except for a select number of tests (for example, AC-34, AC-43, UR-45, and UR-46) that were permeated while confined at 241 kN/m^2 (35.0 psi). In addition, an attempt to standardize the gradient at which the leachate permeated through the samples was vigorously pursued. However, several factors hindered total standardization of the gradients including (1) the height of the samples due to certain limitations; and (2) cases that dictated the use of lower gradients (i.e., permeability was too high so gradient had to be adjusted downward). Generally, a differential total head of approximately 172 kN/m^2 (25 psi) was used for all samples except those with extremely high permeabilities (greater than 1.0 x 10^{-6} cm/sec, e.g., all sodium silicate samples).

∘ Permeation with Chemical Leachate

After an equilibrium water permeability (i.e., baseline permeability) was established, the samples were then permeated with their selected chemical leachate. The net confining pressure was held constant for all tests. Permeation with the chemical leachate continued until an equilibrium permeability was established and a minimum of 2.0 pore volumes had passed through the sample. Many times, after chemical degradation of the sample had taken place, the permeability was of such a magnitude that the testing could not be run continuously. Therefore, intermittent percolation periods with varying interludes, generally one to ten days, proceeded until two successive periods yielded similar permeabilities. After the initial chemical equilibrium permeability was established, the gradient of some samples was reduced to a level one fifth of the original gradient. Once again, the equilibrium permeability was determined according to the standards set forth for chemical permeation.

- Dismantling the Permeameter

After testing was completed according to the criteria set herewith, the permeameter was carefully taken apart. Any pertinent information related to the grouted soil sample and/or permeameter was recorded. In addition, photographs were taken of each sample and any other relevant observations were made (see Figure 21 for instance).

CHEMICALS AND HAZARDOUS LEACHATES USED

Initial Selection of Chemicals to be Studied

Three matrices were developed by Spooner et al. (1982) which summarized the known interactions between grouts and chemical groups. Their matrices particularly set forth the effects of sixteen general classes of organic and inorganic compounds on (a) the set time of grouts and (b) the durability of grouts. The sixteen chemical groups included:

1. Alcohols and glycols
2. Aldehydes and ketones
3. Aliphatic and aromatic hydrocarbons
4. Amines and amides
5. Chlorinated hydrocarbons
6. Ether and epoxides
7. Heterocyclics
8. Nitriles
9. Organic acids and acid chlorides
10. Organometallics
11. Phenols
12. Organic esters
13. Heavy metal salts and complexes
14. Inorganic acids
15. Inorganic bases
16. Inorganic salts

Spooner et al. (1982) pointed out that "the choice of the 16 basic groups was not meant to be all-inclusive, but rather a representative choice of the types of compounds found in landfills." Their report also addressed 12 types of grouts including:

1. Bitumen
2. Portland cement
    a. Type I
    b. Types II and V
3. Clay (bentonite)
4. Clay-cement
5. Silicate

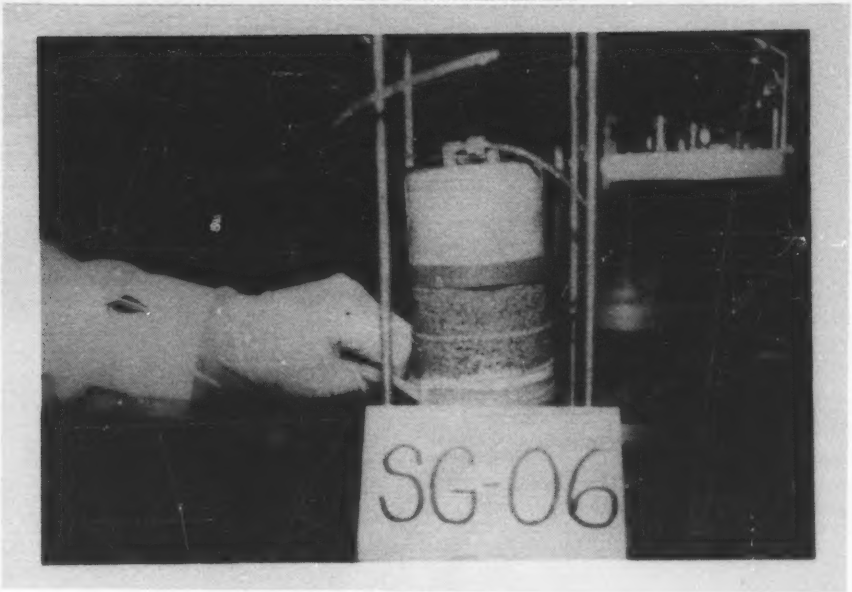


Figure 21. Dismantling of glyoxal-modified sodium silicate sample following permeation with deionized water.

6. Polymers
    a. Acrylamides
    b. Phenolic
    c. Urethane
    d. Urea-formaldehyde
    e. Epoxy
    f. Polyester

A study covering the compatibility of even one grout with the thousands of chemicals and chemical mixtures to be found at a disposal site would be time and cost prohibitive. From a preliminary study of existing lieterature, a grout-chemical matrix was established for this study. Each phase examined different grouts but essentially the same chemicals were used throughout although the concentrations varied. In order to put the study in proper perspective, the matrices established by Spooner et al. (1982) have been modified to include only the chemical groups and grouts employed in this study. These are represented in Tables 4 through 6. As can be seen, the knowledge on grout/chemical compatibility was limited in 1982, the year this study began. For this study, ten representative chemicals were selected which covered the more common waste effluents of larger industries. Eight of these organic and inorganic compounds represent a particular functional group as set forth by Spooner et al. (1982) and are listed in Table 7. In addition a real site refinery waste and a real site paint waste were included in the testing program of Phase II. The real site wastes were obtained as leachates from lysimeter studies conducted at the Center Hill Solid and Hazardous Waste Research Facility by Stamm, Vogt, and Walsh (1985).

Tables 8 through 10 describe the grout/chemical matrices studied during Phases I through III of this study, respectively. Spooner et al. (1982) describe most of these chemical compounds in some detail. The reader is referred to that report for further information on the chemical structure and properties that separate and distinguish these chemical groups.

Concentrations of the Leachates Used

This was an area for which little guidance was available. Spooner et al. (1982) found from their literature review on grout/chemical compatibility that "most of the information detailed the effects of pure chemicals or did not specify a concentration." They assumed in the latter case that the data referred to the effects of undiluted chemicals. They also noted that "while leachates generally contain low levels of compounds, there can be instances where grouts will come into contact with high concentrations of chemicals, such as organic solvent lenses within the groundwater system." In a 1983 report by Larson and May, the effects of groundwater dilution were taken into account. They noted the following:

> ...organic and inorganic compounds, if improperly disposed of, have sufficiently low viscosity to infiltrate soil materials and enter the groundwater. Once in the groundwater, even those wastes considered insoluble could have soluble constituents or additives. The factors of migration and groundwater contamination are different for every disposal site depending on such factors as soil absorption, groundwater flow, etc.

TABLE 4. INTERACTIONS BETWEEN GROUTS AND GENERIC CHEMICAL CLASSES

Chemical Group	Bitumen	Clay-cement	Silicate	Acrylamide	Urethane
Acid	?a	?c	a	c	c
Base	?a	?d	c	d	?d
Heavy Metal	?d	c	?	?	?

(Modified, after Spooner et al. (1982), p. 72)

Key: Compatibility Index

Effect on Durability

a	No significant effect
b	Increase durability
c	Decrease durability (destructive action begins within a short time period)
d	Decrease durability (destructive action occurs over a long time period)
?	Data unavailable

TABLE 5. INTERACTIONS BETWEEN GROUTS AND SPECIFIC CHEMICAL GROUPS

Chemical Group	Bitumen	Clay-cement	Silicate	Acrylamide	Urethane
Alcohols, Glycols	?a	?d	?	?d	a
Aldehydes, Ketones	?d☐	?	?a	?	?d
Aliphatic & Aromatic Hydrocarbons	?d	?	?	?a	?a
Amides & Amines	?	?	?	?	?
Heavy Metal Salts & Complexes	?d	c	?	?	?
Inorganic Acids	?a=	?c	a	c	c
Inorganic Bases	?a	?d	c	d	?d

(Modified, after Spooner et al. (1982), p. 75)

Key: Compatibility Index

Effect on Durability
- a No significant effect
- b Increase durability
- c Decrease durability (destructive action begins within a short time period)
- d Decrease durability (destructive action occurs over a long time period)
- ? Data unavailable
- = Except concentrated acids
- ☐ Except aldehydes which yield an 'a' response

TABLE 6. PREDICTED GROUT COMPATIBILITIES

Chemical Group	Silicate	Acrylamide	Urethane
Alcohols, Glycols	a	-	-
Aldehydes, Ketones	a	?	-
Aliphatic & Aromatic Hydrocarbons	d	-	-
Amides & Amines	a	d	a
Heavy Metal Salts & Complexes	a	?	?
Inorganic Acids	-	-	-
Inorganic Bases	-	-	?

(Modified, after Spooner et al. (1982), p. 77)

Key: Compatibility Index

Effect on Durability
- a No significant effect
- b Increase durability
- c Decrease durability (destructive action begins within a short time period)
- d Decrease durability (destructive action occurs over a long time period)
- ? Data unavailable

TABLE 7. BASIC CHEMICALS USED AS PERMEANTS IN PHASES I, II, AND III

Functional Group	Representative Chemical of Functional Group Used as a Permeant
Alcohols and Glycols	Methanol (alcohol) Ethylene Glycol (glycol)
Aldehydes and Ketones	Acetone
Aliphatic and Aromatic Hydrocarbons	Xylene (mixed isomers)
Amines and Amides	Aniline
Heavy Metal Salts and Complexes	Cupric Sulfate
Inorganic Acids	Hydrochloric Acid
Inorganic Bases	Sodium Hydroxide

TABLE 8. CHEMICAL LEACHATE/GROUT MATRIX FOR PHASE I WITH SAMPLE IDENTIFICATION

Grout	Urethane	Acrylamide AV-100
Leachate		
100% Acetone		AV-01 AV-06
Deionized Water	UR-04	AV-07 AV-08

TABLE 9. CHEMICAL LEACHATE/GROUT MATRIX FOR PHASE II WITH SAMPLE IDENTIFICATION

Grout Leachate	Cement-Bentonite (Mix 1)	Cement-Bentonite (Mix 2)	Sodium Silicate	Urethane	Acrylate AC-400
100% Acetone	CB-10	CB-28	SS-08 SS-14	UR-07 UR-09 UR-10 UR-25	AC-03 AC-04
Reagent grade Aniline		CB-30		UR-20 UR-21	
20% Cupric Sulfate		CB-18 CB-19 CB-29		UR-26 UR-29	AC-22 AC-23
100% Ethylene Glycol	CB-03		SS-11 SS-13	UR-01 UR-14	AC-01 AC-11
4N Hydrochloric Acid		CB-22		UR-22 UR-28	AC-24 AC-28
100% Methanol	CB-14	CB-31		UR-11 UR-13	AC-07 AC-10 AC-12
Real-site Refinery Waste	CB-13		SS-4B SS-6B SS-09	UR-5B UR-6B	AC-05 AC-13
Real-site Paint Waste	CB-08		SS-3B SS-5B SS-10	UR-3B UR-4B	AC-06 AC-19
25% Sodium Hydroxide		CB-23 CB-26		UR-19 UR-23	AC-20 AC-21
100% Xylene	CB-09 CB-11 CB-12		SS-07 SS-12	UR-08 UR-12 UR-15	AC-02 AC-09

TABLE 10. CHEMICAL LEACHATE/GROUT MATRIX FOR PHASE III WITH SAMPLE IDENTIFICATION

Grout Leachate	Acrylate AC-400	Sodium Aluminate-Modified Sodium Silicate	Glyoxal-Modified Sodium Silicate	Urethane
25% Acetone	AC-25 AC-26			
100% Acetone	AC-42 AC-43			
Reagent grade Aniline	AC-40 AC-41			
10% Cupric Sulfate	AC-30 AC-44			
20% Cupric Sulfate		SA-06 SA-07	SG-01 SG-02	
25% Ethylene Glycol				UR-38 UR-39
1N Hydrochloric Acid	AC-38 AC-39			UR-36 UR-37
25% Methanol	AC-27 AC-29			
100% Methanol	AC-45 AC-34			
10% Sodium Hydroxide				UR-40 UR-41
25% Sodium Hydroxide		SA-08 SA-09	SG-07 SG-08	UR-44 UR-45
100% Xylene		SA-02 SA-05	SG-03 SG-04	UR-46 UR-47
Deionized Water	AC-36 AC-37	SA-03 SA-04	SG-05 SG-06	UR-42 UR-43

In this study groundwater dilution was assumed to be 10 to 1 by weight to waste chemical.

Other researchers such as Anderson (1982); and Lord, Weist, Koerner, and Arland (not dated) have used varied leachate concentrations in clay/chemical and grout/chemical compatibility tests.

Over the three phases of this study a number of chemical concentrations have been used in order to define the performance of the grouts under the limits to be expected in chemical concentrations. The chemical concentrations used have been set forth in Tables 8 through 10.

Preparation of Deionized Water and Chemical Permeants

The deionized water was obtained from an in-house system at the Center Hill Solid and Hazardous Waste Research Facility. The system consisted of one No. 2952 organic removal filter and two No. 2951 mixed bed deionizing units. The system was designed to provide 15 to 18 megohm quality at a maximum flow rate of five gallons per minute.

The chemical permeants were, for the most part, used in their as-received condition and concentrations. The exceptions were cupric sulfate, hydrochloric acid, and sodium hydroxide. Table 11 lists the leachates, concentrations upon receipt, mixing details followed where appropriate, and sample identification information for each.

DATA PROCESSING

This study generated volumes of data concerning permeability and reactivity of grouted samples when exposed to deionized water and various chemical leachates. This raw data was entered into desktop computers utilizing a program generated during this study that performed the following:

1) Raw data was recorded on a magnetic floppy disk
2) Permeability calculations were computed utilizing stored calibration data based on the Center Hill testing equipment
3) Numerical hardcopy printouts (in two formats) and plotted versions of data could be generated as needed.

The computing system consisted of the following equipment:

1) Apple IIe desktop computer with 128 k extended memory
2) Zenith monochrome monitor
3) Apple "Duo-Disk" disk drive
4) Apple numeric keypad "IIe"
5) Hewlett-Packard HP7475 "A" plotter

TABLE 11. PREPARATION DETAILS FOR LEACHATES USED IN PHASES I, II, III

Leachate	Format When Received	Desired Concentration	Mixing Instructions
Deionized Water	See text on in-house system	—	—
Acetone	Received at 100% concentration	100%	Used as received
Acetone	Received at 100% concentration	25%	25% mixture by volume, mixed with deionized water
Aniline	Received at 100% concentration	100%	Used as received
Cupric Sulfate	Received as crystals	20%	200g of $CuSO_4$ per liter of deionized water, mixed 3 hours
Cupric Sulfate	Received as crystals	10%	100g of $CuSO_4$ per liter of deionized water, mixed 3 hours
Ethylene Glycol	Received at 100% concentration	100%	Used as received
Ethylene Glycol	Received at 100% concentration	25%	25% mixture by volume; mixed with deionized water
Hydrochloric Acid	Received at 12N strength	4N	33% mixture by volume; acid slowly added to deionized water; heat of hydration controlled by cooling water
Hydrochloric Acid	Received at 12N strength	1N	8.33% mixture by volume; acid slowly added to deionized water; heat of hydration controlled by cooling water

TABLE 11. PREPARATION DETAILS FOR LEACHATES USED IN PHASES I, II, III (CONTINUED)

Leachate	Format When Received	Desired Concentration	Mixing Instructions
Methanol	Received at 100% Concentration	100%	Used as received
Methanol	Received at 100% Concentration	25%	25% mixture by volume; methanol added to deionized water
Sodium Hydroxide	Received at 50% concentration in water solution	25%	50% mixture by volume; NaOH slowly added to deionized water
Sodium Hydroxide	Received at 50% concentration in water solution	10%	20% mixture by volume; NaOH slowly added to deionized water
Xylene (Mixed Isomers)	Received at 100% concentration	100%	Used as received
Real site Refinery Waste	Leachate from lysimeter tests conducted at the Center Hill Lab	——	Used as received
Real site Paint Waste	Leachate from lysimeter tests conducted at the Center Hill Lab	——	Used as received

SECTION 5

RESULTS AND ANALYSIS

If grout barriers are to be considered for bottom or side cutoffs around hazardous waste sites, then the grouts to be used must have low permeability with water and must also resist major changes in their permeabilities when exposed to chemical leachates. This research project investigated the permeability and reactivity of various grouts, both with water and selected chemicals, in order to determine their potential usefulness in grout barriers.

In this chapter, the results of a series of permeability and reactivity tests and their analyses are presented. An analysis that compares the results from the two test series is also presented.

The permeability test program involved tests on grouted soil samples, first with water to obtain their baseline permeabilities, then with the selected chemicals to find out if there were any changes in their permeabilities, and if so, how large they were.

The reactivity tests were immersion-type resistivity tests conducted to observe the destructive effect of chemicals on small grouted soil cylinders, and to see if any correlation exists between the results from the reactivity and permeability tests.

The laboratory permeability test is the most direct test used to determine the behavior of the permeability of a grout with chemicals. It is also time consuming and expensive. The immersion-type reactivity test with chemicals, on the other hand, is less expensive and may be quicker. It is a test of durability and, as such, its results on a grout may relate to the permanence of its permeability. A definite correlation would facilitate the evaluation of a proposed grout with the chemicals at a site.

In the following sections, the permeability test results for seven different grouts, and the results of reactivity tests for four different grouts are presented. In addition, the results were compared to find if any correlation exists between them.

PERMEABILITY TESTS

In this part of the test program permeability tests were conducted on grouted soil samples, first with water to obtain their baseline permeabilities, then with various chemicals to measure the changes they may cause in sample permeabilities. In addition, the effects of chemical concentration on the permeability of the grout samples were also investigated.

The permeability tests were conducted in triaxial type permeameters, using 75 mm diameter samples. The sample thicknesses varied between 24 and 118 mm. The falling-head type permeameters, with both a headline (inflow) and a tailline (outflow), were used to measure the permeability of each sample. Generally, auxiliary air pressures (headpressure and tailpressure) were used to increase and control the driving pressures. The driving gradient was typically calculated by dividing the difference between the headpressure and tailpressure by the sample thickness. The net confining pressure (or effective confining pressure) was defined as the difference between the confining chamber pressure and the average of the headpressure and tailpressure. The sample permeabilities were calculated using the initial and final total head differences, the time increment, sample area and length, headline and tailline cross-sectional area, and the falling-head permeability formula.

The results of permeability tests are presented as plots of permeability versus flow. The sample permeabilities are plotted on a log scale in cm/sec, while the flow is plotted in terms of pore volumes. Each test reading is represented by a + or x mark. An elapsed time scale is also shown on the top of each plot. However, since the permeability of most samples changed with chemical flow, the time scale is often not linear.

The legend block of the permeability plots shows the total test time that the sample was actively tested, the number of days that it was tested with water, and the type of chemical used. Also, it references the symbols used to mark the test points with water and with chemical (i.e., the +'s and x's).

For purposes of flow calculations the pore volume of a grouted sample was defined as the total volume of the pores in the soil medium without the injected grout. The reason for using this fictitious volume was that the true volume of pores in a grouted sample could not be determined. Some preliminary tests on a sand sample grouted with acrylate grout indicated that the real pore volume of the grouted sample may only be one-third to one-half of that of the pure sand.

Most permeability test figures in the text show two plots, one for each of the replicate samples on the indicated chemical. In some cases three samples were tested and therefore all three test plots are presented on successive pages. In other figures the results of only one test are shown; in part (a) the permeability versus flow plot with water, and in part (b) the permeability versus flow plot with the designated chemical. This format allows the viewing of the plot with water on a larger scale when the sample has a large pore volume flow on chemical and the water portion of the plot would otherwise be squeezed together and could not be properly distinguished.

As was required by the standard test procedure, at least two replicate samples were tested for each selected grout and chemical combination. In case of inconsistent results one or more samples were tested for the same combination. For some cement-bentonite (mix 1) grout and chemical combinations only one sample each was tested because their permeabilities were too high for their use in grout barrier construction, and continued testing was not warranted. On the other hand, certain cement-bentonite (mix 2) samples were tested without a replicate because their permeabilities were very low (in some cases as low as 3×10^{-11} cm/sec) and required long testing times. Consequently, some of the test stations were tied up longer than planned and this eliminated the testing of some of the replicates.

Each permeability test sample was first tested with deionized water to determine its baseline permeability. It was attempted to conduct this portion of testing until at least one pore volume of flow passed through the sample, or the sample came to equilibrium with water. Equilibrium was assumed to have been reached when the permeability versus pore volume flow plot had leveled off.

The introduction of the chemical usually upset the equilibrium that the sample reached with water. The plot commonly showed an increase in permeability with increasing flow, until a new equilibrium with the chemical was reached.

The following sections present the results and analyses of permeability tests on the following grouts: acrylate, cement-bentonite (mix 1), cement-bentonite (mix 2), sodium silicate, glyoxal-modified sodium silicate, sodium aluminate-modified sodium silicate, and urethane.

Permeability Tests of Acrylate Grout

Acrylate grout was selected as one of the first test grouts in this study. It was chosen because of its many attractive qualities, some of which are nontoxicity, low viscosity (so it can penetrate a fine sand), ease of use, adequately long set time that will not interfere with grouting operations, relatively quick hardening with little curing time, very low and consistent permeability with water ($k = 5.0 \times 10^{-10}$ cm/sec) and high mechanical strength to resist erosion.

In this research the acrylate grout samples were made by injecting the grout into medium silica sand. The mixing and injecting of the grout was a relatively simple operation. The samples made were very consistent with respect to appearance and permeability. The color of the samples was grayish white. Their consistency was that of a hard rubber. Because of their low permeability, the samples were made to be thin (about 34 mm thick), and they were tested at high gradients (between 105 and 804) so that the tests could be finished on schedule. To make sure that the effect of these high gradients would not be confounded with the effect of the chemicals, the samples were tested with water over an extended period using these high gradients and were found to withstand them without deterioration.

In this study the permeability of the acrylate grout was tested with deionized water, 100% and 25% solutions of acetone, reagent grade aniline, 20% and 10% solutions of cupric sulfate, 100% solution of ethylene glycol, 4N and 1N solutions of hydrochloric acid, 100% and 25% solutions of methanol, real-site paint waste, real-site refinery waste, 25% solution of sodium hydroxide, and reagent grade xylene. In each case, two or more samples were tested with every permeant.

- Permeability Test of Acrylate Grout With Deionized Water

All acrylate grout samples were permeated with deionized water in order to saturate them prior to subjecting them to chemical leachates. Originally it was intended to test the samples with water until they reached equilibrium, or through at least one pore volume of flow. In the case of the acrylate grout these criteria could not be met for every sample because of lack of time and available test stations. However, these writers believe that all acrylate samples tested were at least near their equilibrium permeability with water when the chemicals were introduced.

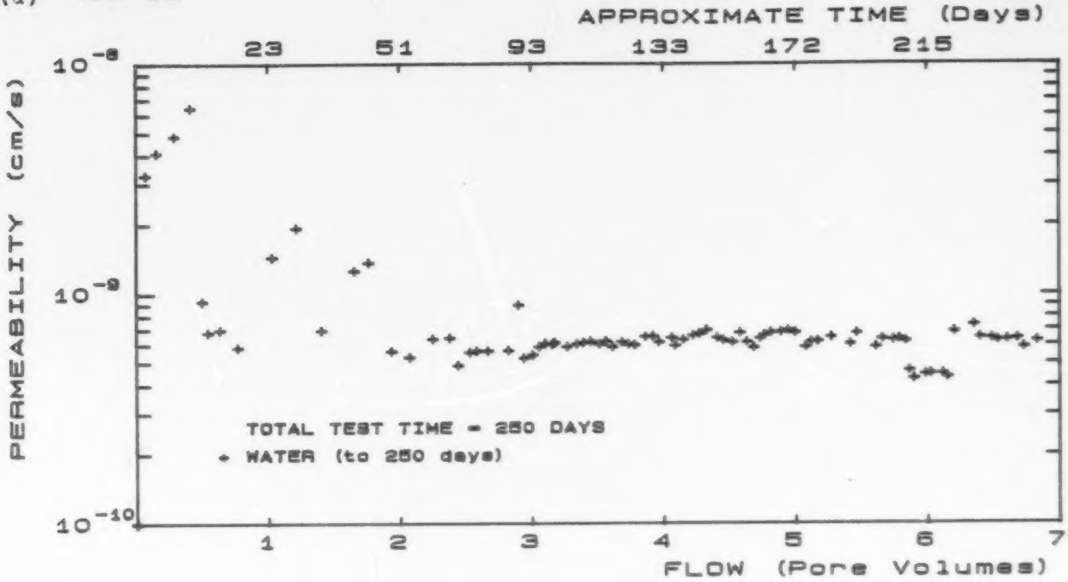
To obtain the average permeability of acrylate grout with water, the permeability data with water for 26 samples were analyzed. For each sample, the average of the last five readings with water were computed, and then used to determine the overall average and median values of permeability for the 26 samples. The average permeability with water was 5.1 x 10^{-10} cm/sec, and the median value was 5.0 x 10^{-10} cm/sec.

In addition, two acrylate grout samples, designated as AC-36 and AC-37, were tested with water over an extended time to thoroughly investigate their behavior with water. Both samples had a thickness of 34 mm and a diameter of 75 mm. In testing sample AC-36, a gradient of 320 was used for the first 0.42 pore volume of flow, a gradient of 414 to a pore volume flow of 0.78, and 517 for the rest of the test. In the major segment of the test, a headpressure of 242 kPa (35 psi), a tailpressure of 69 kPa (10 psi), and an effective confining pressure of 121 kPa (17.5 psi) were used. For sample AC-37, the starting gradient of 310 was used for the first segment of 0.13 pore volume of flow, 414 to the accumulated flow of 0.47 pore volume, and 517 to the end of the test. Once the gradient was raised to 517, the pressure conditions on the sample were identical to those described for sample AC-36.

Figure 22 shows the permeability versus pore volume flow plots for the two samples. It can be seen that, after initial fluctuations, the samples settled down to their equilibrium permeabilities of approximately 6 x 10^{-10} and 5.7 x 10^{-10} cm/sec, respectively. These are low values that were typically obtained for acrylate grouts. For sample AC-36, equilibrium was reached at an approximate flow of 2.0 pore volumes, while for sample AC-37 it occurred at 1.2 pore volumes of flow.

It should be noted that both samples already had their permeabilities approach the final equilibrium values at earlier stages, that is, at pore volume flows of 0.8 and 0.5, respectively. However, at that point the driving pressures and gradients were changed and that caused a temporary upturn in sample permeabilities before they returned to the lower equilibrium values. It appears that the change in the gradients delayed reaching the equilibrium states by about 0.7 to 0.4 pore volume of flow. Therefore, had the gradients not been changed, it is estimated that these samples may have reached equilibrium between 1.2 and 0.8 pore volumes of flow. Using the data from 26 permeability tests on acrylate grout, on the average they achieved equilibrium on water after 0.64 pore volume of flow.

(a) AC-36



(b) AC-37

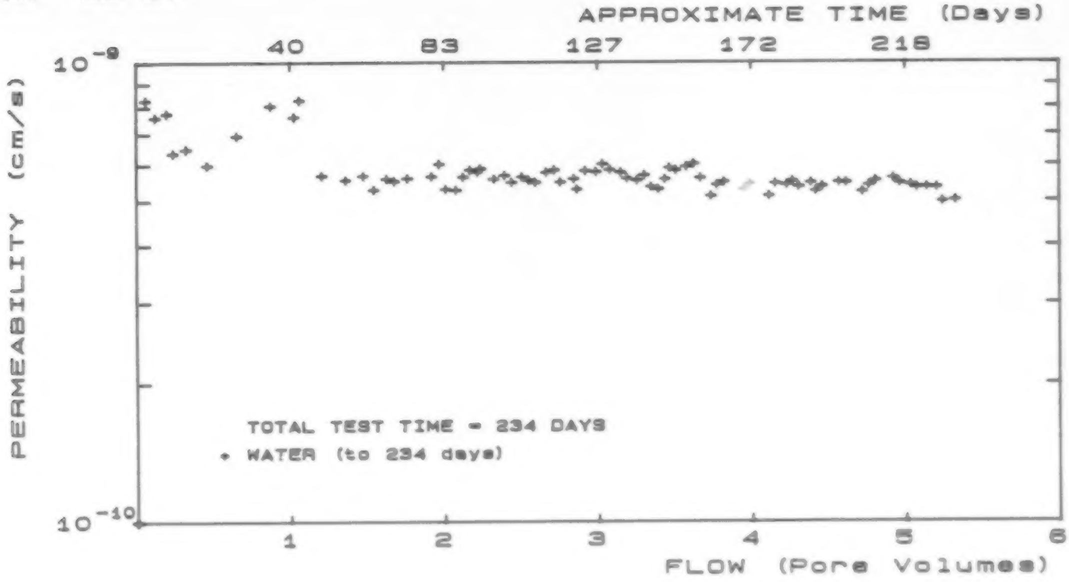


Figure 22. Permeability versus volume of flow of water through acrylate grout. (a) Plot for sample AC-36. (b) Plot for sample AC-37.

Once samples AC-36 and AC-37 reached equilibrium, their permeabilities stayed there without any measurable variation to the end of the tests. These samples were tested over a span of 250 and 234 days, and to 6.8 and 5.4 pore volumes of flow, respectively.

In summary, the acrylate grouts had exceptionally low permeabilities with water, the average being 5.1×10^{-10} cm/sec. On the average, they reached their equilibrium within 0.7 pore volume of flow, and usually had a stable permeability beyond that.

- Permeability Test of Acrylate Grout With 100% Acetone

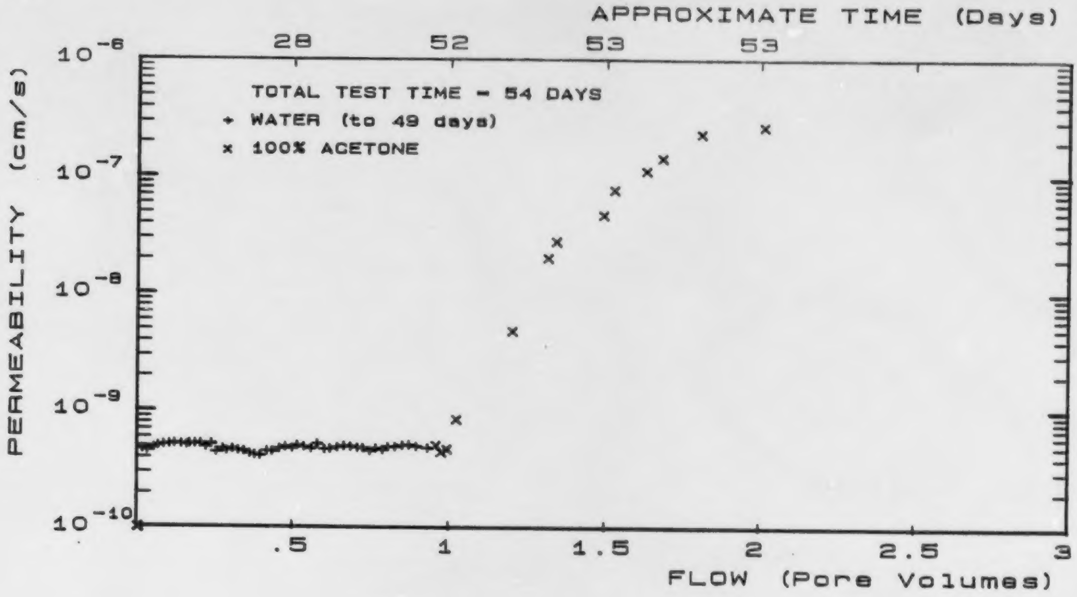
Four acrylate grout samples, AC-3, AC-4, AC-42, and AC-43, were tested with 100% acetone. The AC-3 and AC-4 samples were tested in Phase II of this study, while AC-42 and AC-43 were tested in Phase III. In this section, the test results on samples AC-3 and AC-4 are presented.

The thicknesses of samples AC-3 and AC-4 were 33 and 35 mm, respectively, and both were 75 mm in diameter. Figure 23 shows the permeability test plots for the two samples.

Preceding the introduction of acetone, the two samples were saturated with water. The water permeation for sample AC-3 was, for the most part, accomplished at a net confining pressure of 155 kPa (22.5 psi), a headpressure of 207 kPa (30 psi), and a backpressure of 34.5 kPa (5 psi). The sample was tested at a gradient of 533 for 50 days and to a flow of 0.93 pore volume with water. Water was permeated through sample AC-4 at a headpressure that was first set at 207 kPa (30 psi) and was later changed to 275 kPa (40 psi), at corresponding net confining pressures of 155 kPa (22.5 psi) and 173 kPa (25 psi), respectively, and at a tailpressure of 0. Sample AC-4 was first tested at a gradient of 603 and later at a gradient of 804 for a total of 50 days. The total flow was 0.45 pore volume of water. For sample AC-3, the permeability vs. pore volume flow curve with water equilibrated at a permeability of 5.1×10^{-10} cm/sec. For sample AC-4, equilibrium occurred at a permeability of 1.8×10^{-10} cm/sec.

The 100% acetone was introduced into sample AC-3 at a headpressure of 173 kPa (15 psi), a tailpressure of 34.5 kPa (5 psi), and a net confining pressure of 138 kPa (20 psi). Sample AC-4 was tested on acetone at a headpressure of 138 kPa (20 psi), a tailpressure of 34.5 kPa (5 psi), and a net confining pressure of 121 kPa (17.5 psi). The gradients in the two samples were 426 and 302, respectively. Immediately after the introduction of acetone, the permeabilities of both samples started to rise. The permeability of sample AC-3 gently rose to what appears to be an equilibrium permeability at 2.8×10^{-7} cm/sec after 1.1 pore volumes of flow and four days with acetone. Sample AC-4 behaved somewhat differently. Its permeability also started to rise immediately after the introduction of acetone, but the rate of rise was faster than for AC-3. The sample reached its first peak permeability of 6.4×10^{-7} cm/sec after 1.4 pore volumes of flow of acetone, and from there it jumped to its final permeability of 2.6×10^{-6} cm/sec which occurred after a total flow of 1.5 pore volumes with acetone.

(a) AC-3



(b) AC-4

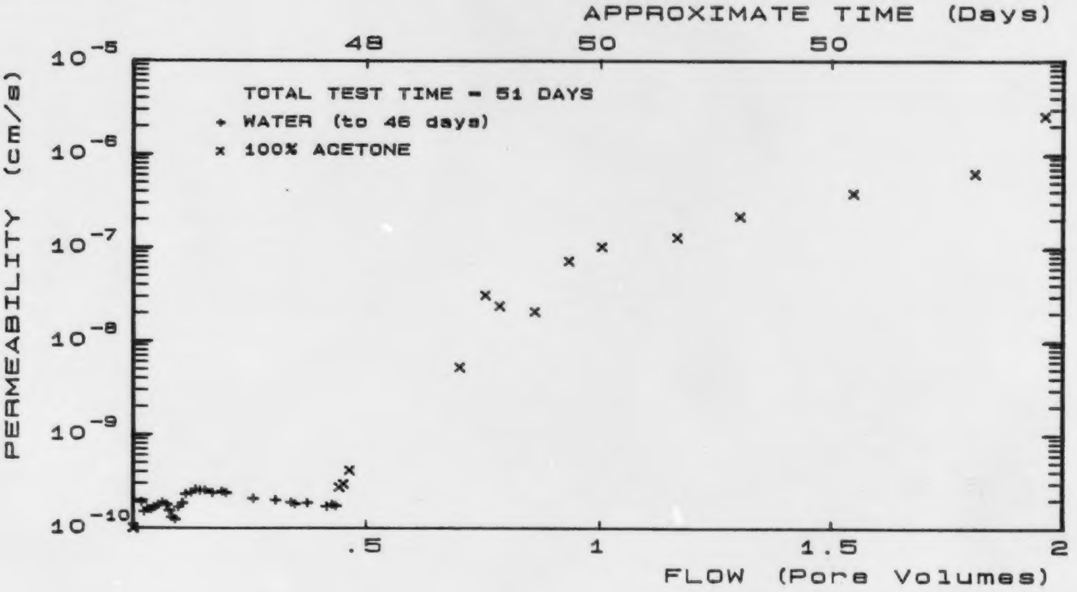


Figure 23. Permeability versus volume of flow of water and 100% acetone through acrylate grout. (a) Plot for sample AC-3. (b) Plot for sample AC-4.

It now seems clear that while the tests were in progress, it was mistakenly assumed from the shape of the permeability versus pore volume flow curves that samples AC-3 and AC-4 had come to an equilibrium. However, from test results for samples AC-42 and AC-43 in Phase III of this project, it appears that samples AC-3 and AC-4 may not have reached a final equilibrium and should have been tested longer. It is believed that the test results for samples AC-42 and AC-43, discussed in the next section, more accurately represent the behavior of acrylate grouts on acetone than those for samples AC-3 and AC-4.

- Acrylate Grout Samples Permeated With 100% Acetone - Phase III

Two acrylate grout samples, designated AC-42 and AC-43, were tested with 100% acetone. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 24 and 25 show the permeability versus pore volume flow graphs obtained for these samples, respectively.

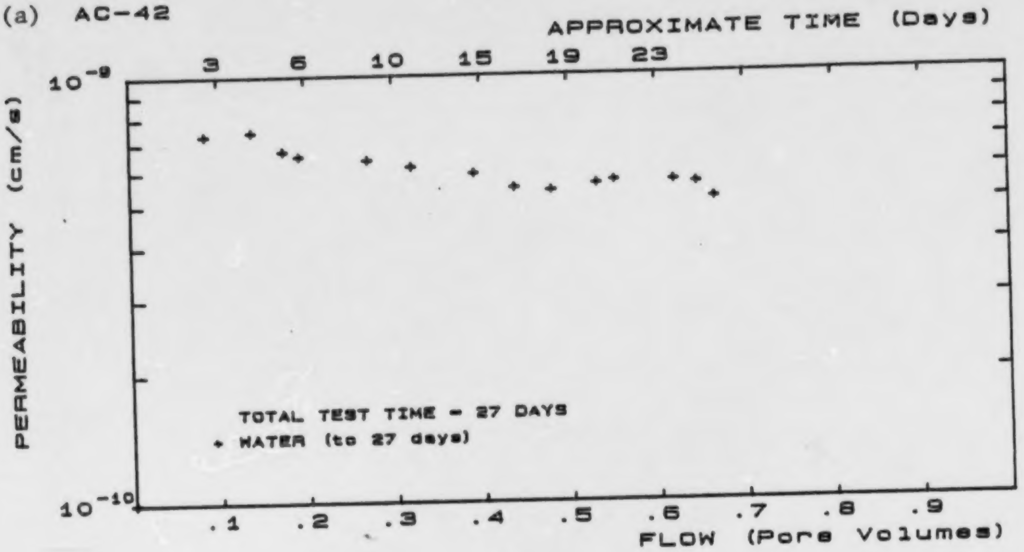
Both samples were initially permeated with deionized water. Sample AC-42 was permeated with water for 26.9 days with a accumulated flow of 0.67 pore volume. Sample AC-43 was tested on water for 46.6 days with an accumulated flow of 1.5 pore volumes. The testing was conducted with net confining pressures of 120.8 and 241.5 kPa (17.5 and 35.0 psi) for AC-42 and AC-43, respectively; a backpressure of zero; and a gradient of 517. The plots of permeability versus flow show little variation in comparison to one another. The curve for AC-42 indicates an equilibrium permeability of 5.8 x 10^{-10} cm/sec compared to 5.6 x 10^{-10} cm/sec for AC-43.

One hundred percent acetone was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi) for AC-42 and 241.5 kPa (35.0 psi) for AC-43, the backpressure was maintained at zero, and the gradient remained at 517. Sample AC-42 was permeated with chemical for 0.15 day with an accumulated chemical flow of 38.8 pore volumes. Sample AC-43 was permeated with 100% acetone for 0.23 day with a sum chemical flow of 45.2 pore volumes. The mode of permeability increases and leachate/grouted soil reactions were nearly identical for AC-42 and AC-43.

Both samples experienced abrupt increases in permeability when permeated with 100% acetone. The only significant difference between the two samples was the initial jump in permeabilities. The permeability of AC-42 increased to 2.2 x 10^{-7} cm/sec which was roughly threefold less than the 6.5 x 10^{-7} cm/sec for AC-43.

The reaction of the grouted soil to 100% acetone was exhibited in two ways: the effluent changed color and a gas began to form. After 0.2 pore volume had entered the grouted sample, the effluent turned from a clear solution to a cloudy orange-yellow fluid. Shortly thereafter a gas began to be emitted from the 3.2 mm (0.125 in.) tubing line at the rate of one bubble every one to three seconds. The effluent discoloration cleared within a matter of three pore volumes to its original state. The gas production dropped off rapidly until it was absent after approximately sixteen to eighteen pore volumes of chemical had passed. Interestingly, when the gradient

(a) AC-42



(b) AC-42

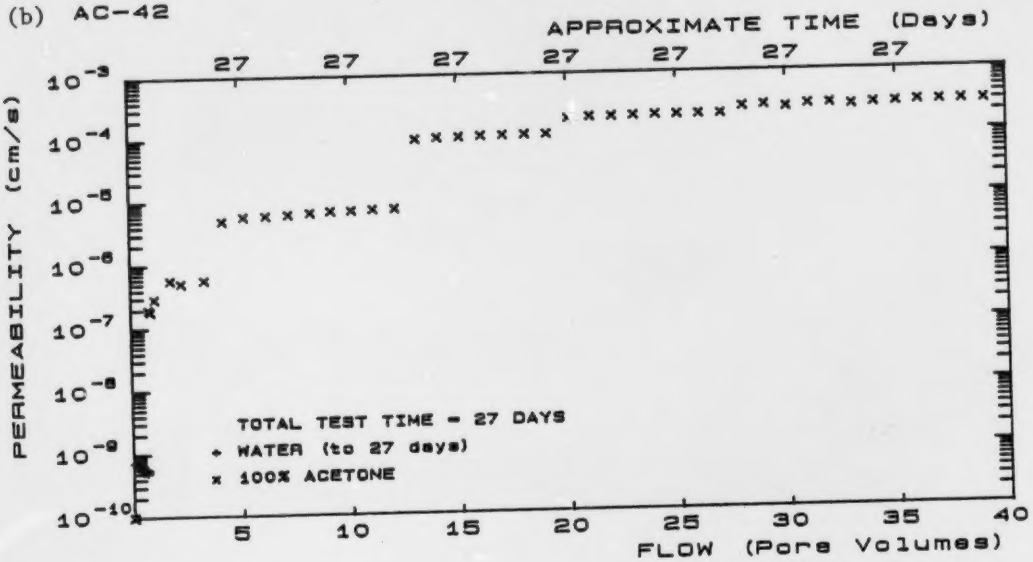
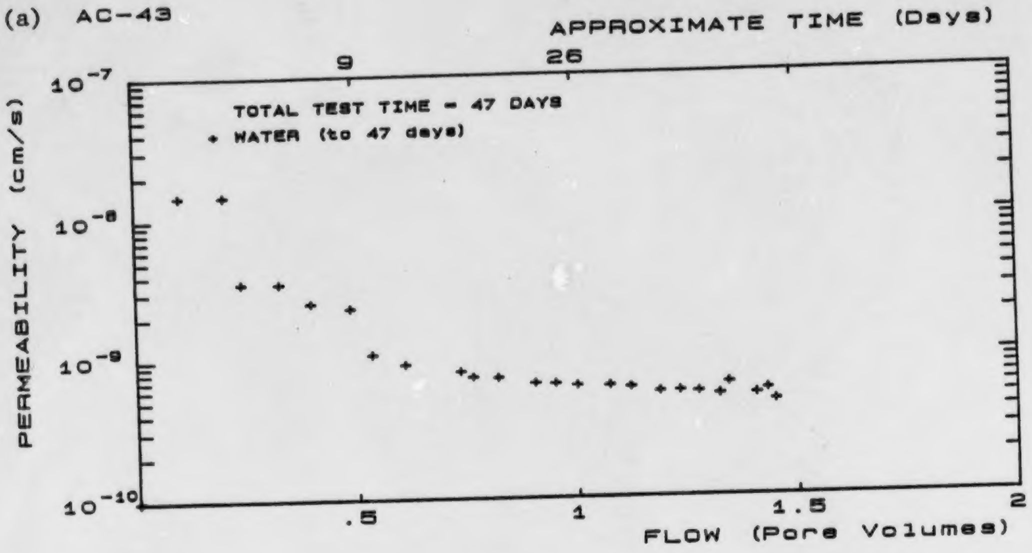


Figure 24. Permeability versus volume of flow through acrylate grout sample AC-42. (a) Water as permeant. (b) Water and 100% acetone as permeants.



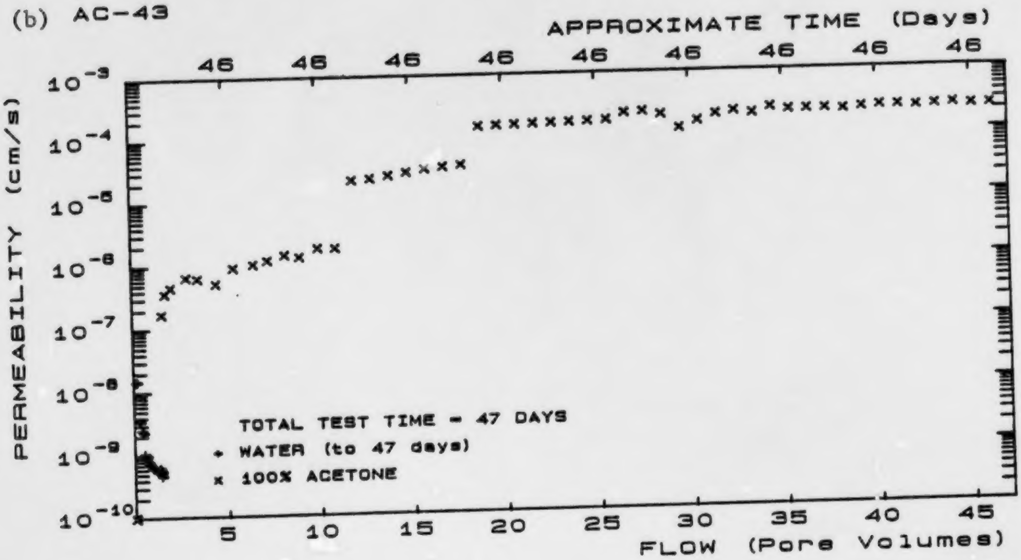


Figure 25. Permeability versus volume of flow through acrylate grout sample AC-43. (a) Water as permeant. (b) Water and 100% acetone as permeants.

was reduced to 131 the production of gas began once more, this time at approximately one half the initial rate. This second period of gas production decreased rapidly but never completely ceased.

The stair-step nature of the permeability versus pore volume flow curves resulted from stopping and restarting the percolation process. During the experiments each percolation period was followed by a time span of generally one to seven days when the permeameter was shut down. A total of six percolation periods with varying rest periods in between extended over approximately nineteen days for AC-42. The last two periods were performed with a reduced gradient of 131. The net confining pressure and backpressure remained unchanged at 120.8 kPa (17.5 psi) and zero, respectively. AC-43 had a total of seven intermittent percolation periods with varying rest periods extending over twenty-six days. The last three periods were performed using a reduced gradient of 131. The net confining pressure remained at 241.5 kPa (35.0 psi), as well as the backpressure at zero. Equilibrium permeability was assumed to be reached when two separate percolation periods yielded similar permeabilities. Based on this criterion, the final equilibrium permeabilities were 2.9×10^{-4} cm/sec for AC-42 and 2.3×10^{-4} cm/sec for AC-43.

○ Acrylate Grout Samples Permeated With a 25% Acetone Solution - Phase III

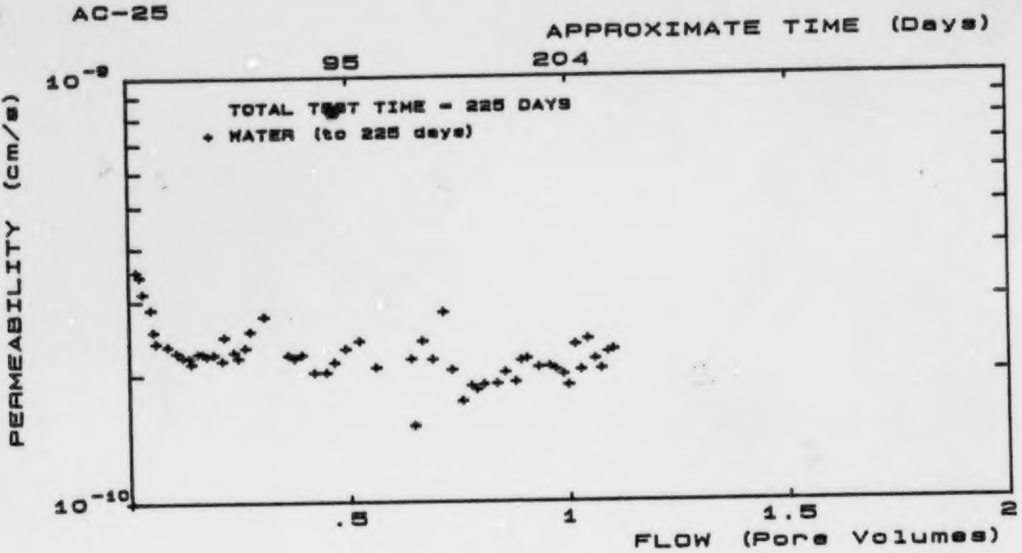
Two acrylate grout samples, designated AC-25 and AC-26, were tested with a 25% solution of acetone in water. Each sample had a diameter of 75 mm. Sample AC-25 had a thickness of 36 mm and AC-26 had a thickness of 30 mm. Figures 26 and 27 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-25 was permeated with water for 225 days with an accumulated flow of 1.1 pore volumes. Sample AC-26 was tested on water for 237 days with an accumulated flow of 1.5 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of 69.0 kPa (10.0 psi). The gradients varied somewhat due to the difference in sample thicknesses. Sample AC-25 had a gradient of 297 and AC-26 had a gradient of 352. The plots of permeability versus flow show little variation. The curve for AC-25 indicates an equilibrium permeability of 2.2×10^{-10} cm/sec as compared to 2.0×10^{-10} cm/sec for AC-26.

A 25% acetone solution was introduced with the net confining pressure, the backpressure, and gradients set equal to those used for tests on water. Sample AC-25 was permeated with the 25% acetone solution for 92.3 days with an accumulated chemical flow of 18.7 pore volumes. Sample AC-26 was permeated with a 25% solution of acetone for 130 days with a sum chemical flow of 32.8 pore volumes.

Both samples exhibited gradual increases in permeability. Over a period of twenty-five days and a leachate percolation of 1.0 pore volume, AC-25 approached a permeability of 1.8×10^{-7} cm/sec. In contrast, AC-26 passed 1.7 pore volumes of leachate over a period of approximately twenty-seven days. Its initial permeability plateau was 6.2×10^{-9} cm/sec which was well over an order of magnitude less than that of AC-25. No explanation for this

(a)



(b)

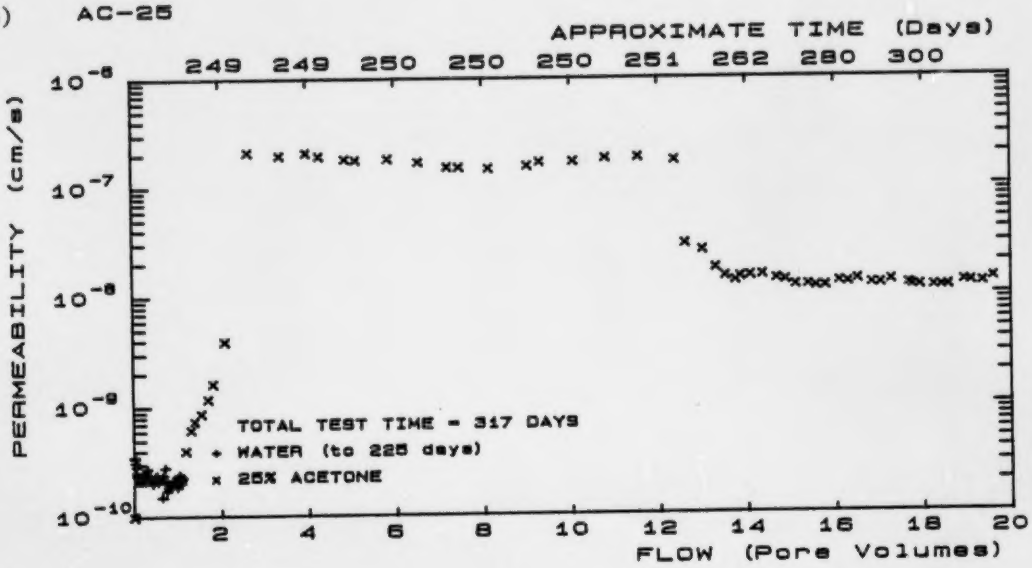


Figure 26. Permeability versus volume of flow through acrylate grout sample AC-25. (a) Water as permeant. (b) Water and 25% acetone as permeants.

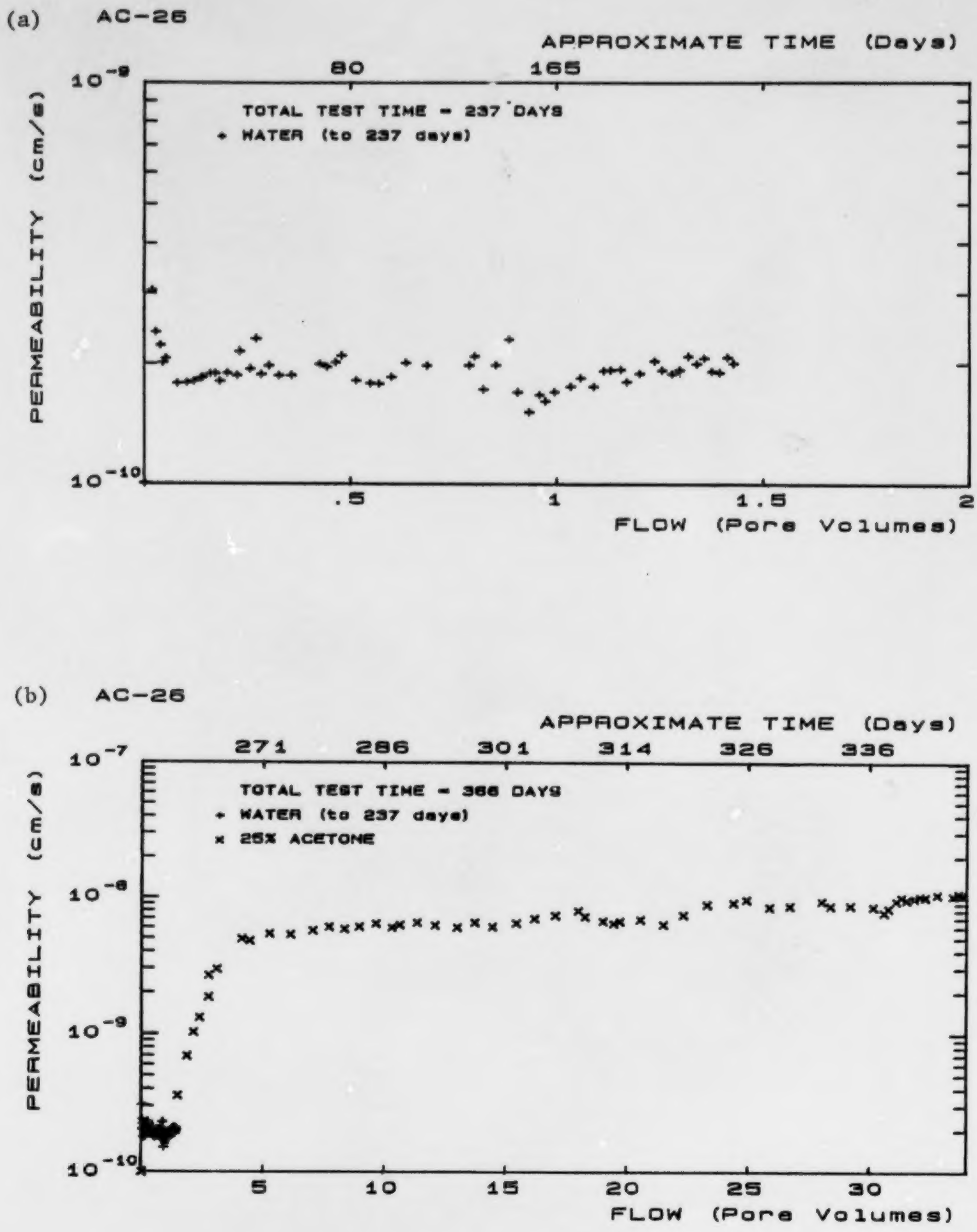


Figure 27. Permeability versus volume of flow through acrylate grout sample AC-26. (a) Water as permeant. (b) Water and 25% acetone as permeants.

behavior can be given at this time.

Sample AC-25 remained at a constant permeability while the gradient remained at 352. But the permeability decreased to 1.3 x 10^{-8} cm/sec when the gradient was reduced to 105, the backpressure was reduced to 34.5 kPa (5.0 psi), while the net confining pressure remained at 120.8 kPa (17.5 psi). It is interesting to note that when the gradient of sample AC-26 was decreased to 124, and the backpressure reduced to 34.5 kPa (5.0 psi), while maintaining the net confining pressure at 120.8 kPa (17.5 psi), the sample yielded an equilibrium permeability of 1.1 x 10^{-8} cm/sec, nearly the same as AC-25. Nevertheless, the difference in their reactions to the 25% acetone solution cannot be explained at this time.

- Acrylate Grout Samples Permeated With Reagent Grade Aniline - Phase III

Two acrylate grout samples, designated AC-40 and AC-41, were tested with reagent grade aniline. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 28 and 29 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-40 was permeated with water for 92.1 days with an accumulated flow of 2.6 pore volumes. Sample AC-41 was tested on water for 109 days with an accumulated flow of 3.5 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of 69.0 kPa (10.0 psi). The gradients for AC-40 and AC-41 were 310 and 517, respectively. The plots of permeability versus flow have roughly the same shape, but the equilibrium permeabilities vary by a factor of nearly two. The curve for AC-40 indicates an equilibrium permeability of 9.6 x 10^{-10} cm/sec as compared to 5.5 x 10^{-10} cm/sec for AC-41.

Reagent grade aniline was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressures and the backpressures were maintained at the levels used for testing with water. The gradient of sample AC-40 was increased to 517, while for AC-41 it was maintained at 517. Sample AC-40 was permeated with chemical for 0.67 day with an accumulated chemical flow of 38.9 pore volumes. Sample AC-41 was permeated with aniline for 5.8 days with a sum chemical flow of 24.5 pore volumes.

Following the introduction of aniline, the permeabilities of the samples increased abruptly by nearly three orders of magnitude. The permeability of sample AC-40 increased from 9.6 x 10^{-10} to 1.8 x 10^{-6} cm/sec after 0.5 pore volume and 9 days of permeation with aniline. The increase in permeability of sample AC-41 was similar in magnitude, but occurred after 1 pore volume and 6 days of permeation with aniline.

Sample AC-40 experienced three abrupt, but relatively small increases in permeability following the initial large increase. The abrupt increases occurred after 15, 20, and 27 pore volumes had flowed through the sample. Permeabilities remained roughly constant during the periods between the abrupt changes. In contrast, the permeability of sample AC-41 increased constantly, but at varying rates, following the initial large increase. The abrupt

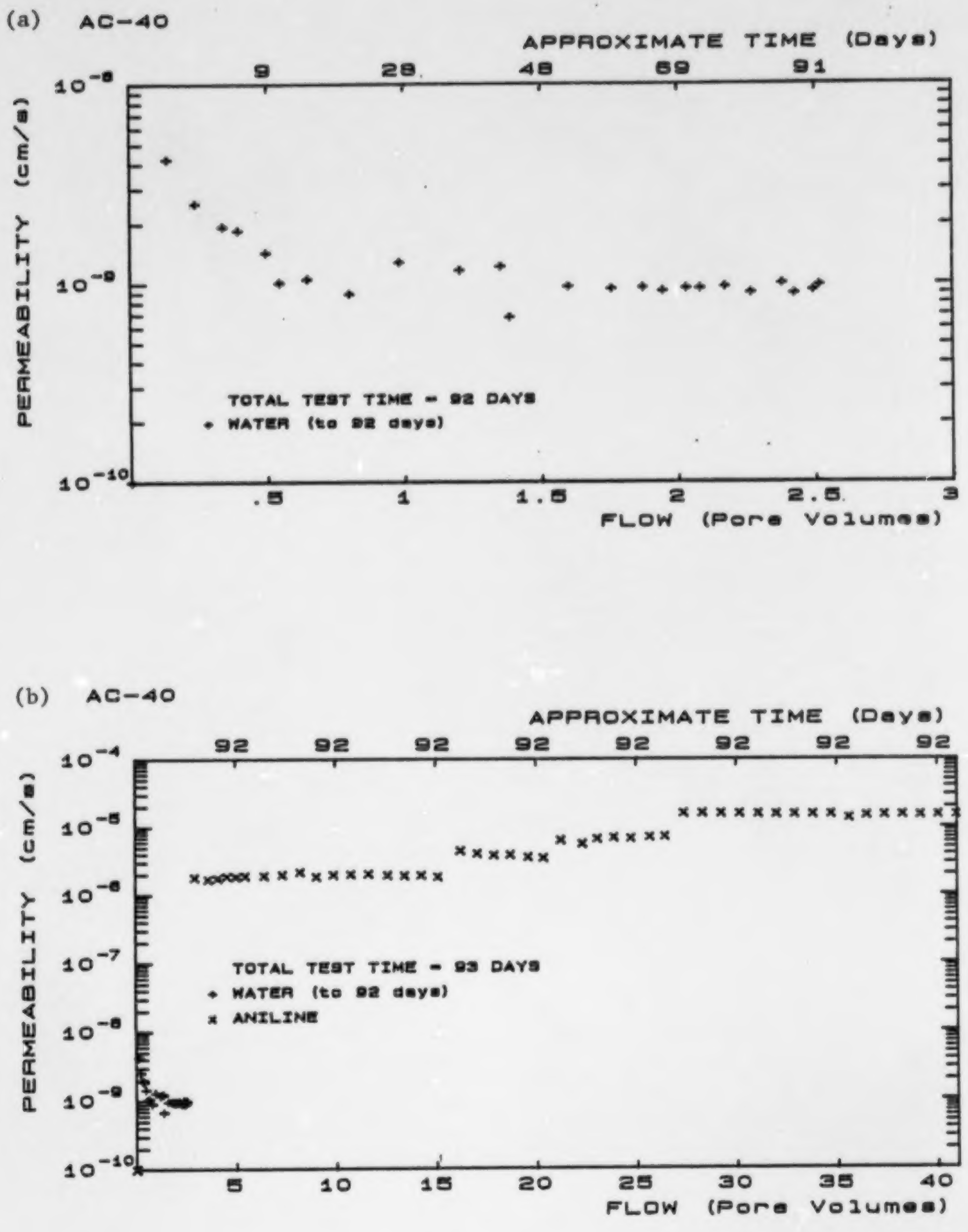


Figure 28. Permeability versus volume of flow through acrylate grout sample AC-40. (a) Water as permeant. (b) Water and aniline as permeants.

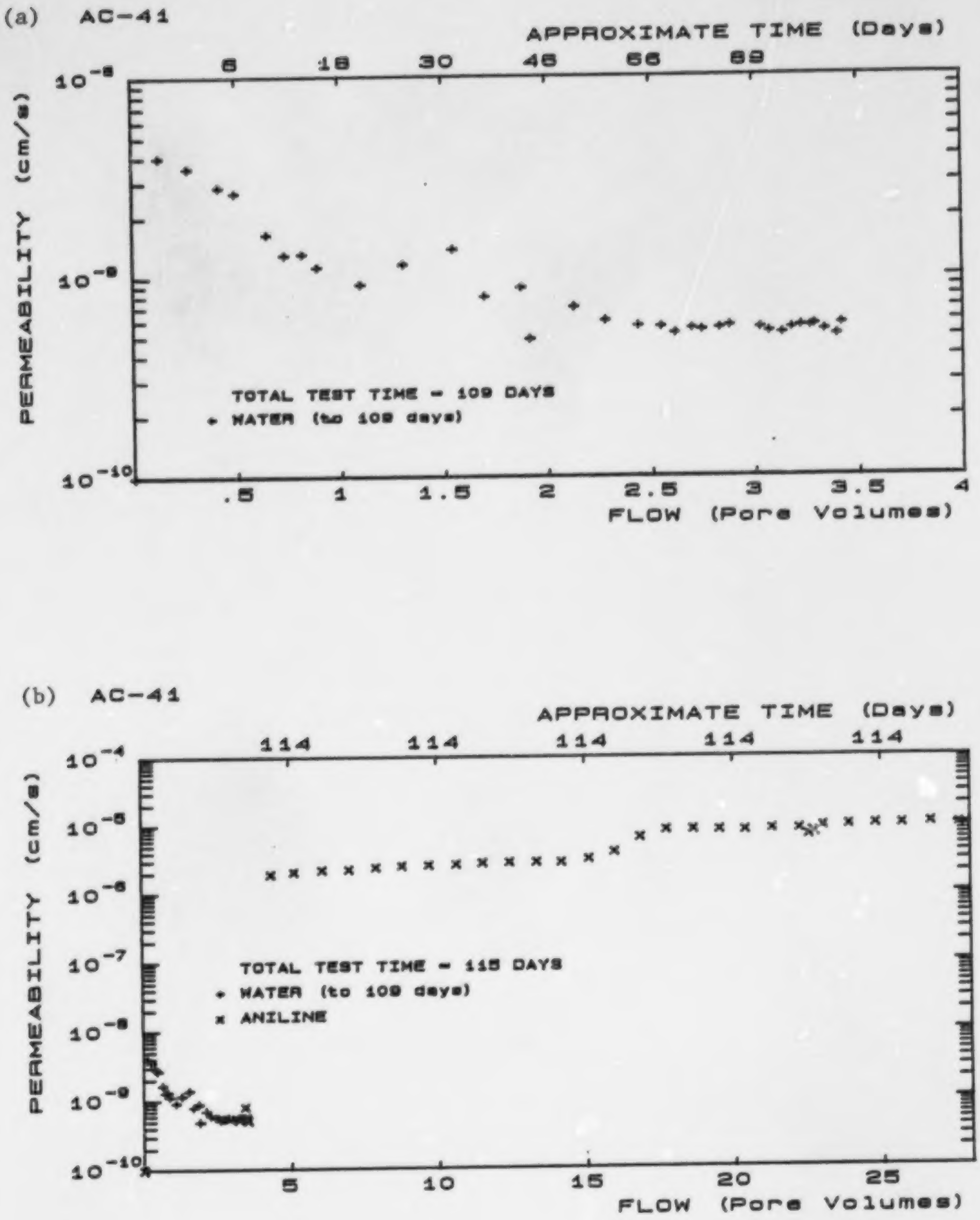


Figure 29. Permeability versus volume of flow through acrylate grout sample AC-41. (a) Water as permeant. (b) Water and aniline as permeants.

stepwise increases in permeability of AC-40 resulted from the percolation process being stopped (shut sample off) for a period of time, generally one to ten days, and then restarted. Final equilibrium permeability was considered to have occurred when two separate percolation periods yielded equilibrium permeabilities of similar magnitude.

Although the plots of permeability versus flow for samples AC-40 and AC-41 are somewhat different in form, they indicate equilibrium permeabilities that are roughly comparable. Sample AC-40 reached an equilibrium permeability of 1.5 x 10^{-5} cm/sec, whereas the equilibrium permeability of sample AC-41 was somewhat less at 9.9 x 10^{-6} cm/sec. In general the introduction of reagent grade aniline increased the permeability of samples of acrylate grout by approximately five orders of magnitude compared to that of water.

- Permeability Tests of Acrylate Grout With 20% Cupric Sulfate

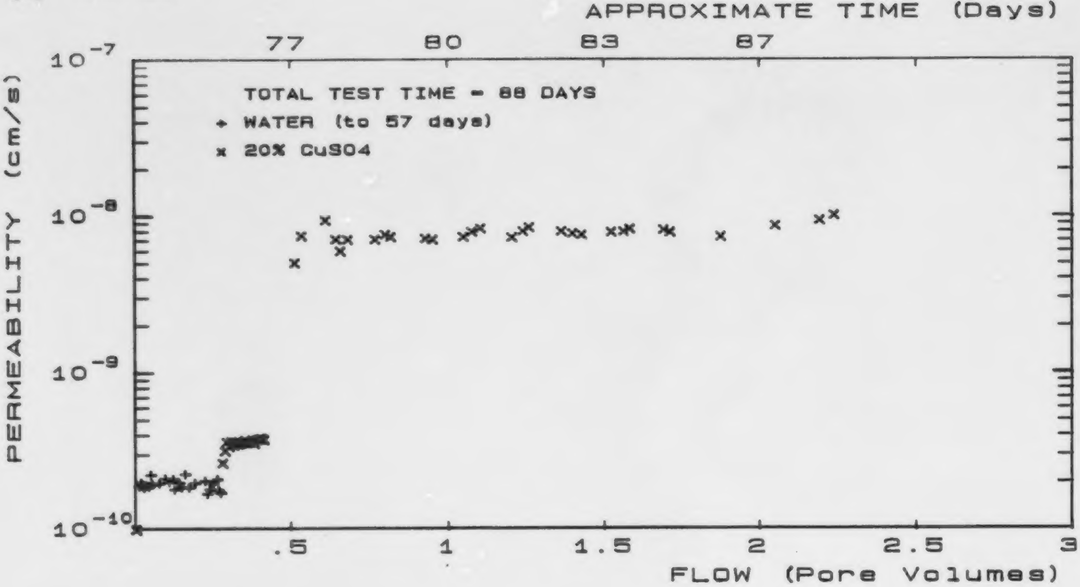
Two acrylate grout samples, AC-22 and AC-23, were tested with 20 percent cupric sulfate. Their thicknesses were 35 and 36 mm, respectively, and both were 75 mm in diameter. Figure 30 shows the permeability test plots for the two samples.

Preceding the introduction of cupric sulfate, the two samples were saturated with deionized water. The water permeation through both samples was accomplished at a net confining pressure of 121 kPa (17.5 psi), a headpressure of 173 kPa (25 psi), and a backpressure of 69 kPa (10 psi). Sample AC-22 was tested at a gradient of 302 for 59 days with an accumulated flow of 0.28 pore volume flow of water, while sample AC-23 was permeated with water for 59 days at a gradient of 293 with an accumulated flow of 0.23 pore volume. Sample AC-22 came to an equilibrium permeability at 1.9 x 10^{-10} cm/sec, sample AC-23 at 1.7 x 10^{-10} cm/sec.

The 20% cupric sulfate was introduced into the samples at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). The gradients in the two samples were maintained at 302 and 293, respectively. After the introduction of cupric sulfate, the permeabilities of both samples started to rise immediately. Sample AC-22 reached its first peak of permeability at 7.5 x 10^{-9} cm/sec, where the sample seemed to have come to an equilibrium with permeabilities between 7.5 and 8 x 10^{-9} cm/sec for over 1.7 pore volumes of flow. The test was terminated after 2.1 pore volumes of flow of cupric sulfate, just when its permeability seemingly began to rise again. Its final permeability was 1 x 10^{-8} cm/sec. Sample AC-23 was tested over a longer period of time and gave somewhat different end results. Its permeability also started to rise immediately after the introduction of cupric sulfate, and the sample reached its first peak of permeability at 3.7 x 10^{-8} cm/sec after 2.1 pore volumes of chemical flow. However, with continued testing, its permeability rose again sharply and then continued to rise slowly to a final equilibrium permeability of 2.3 x 10^{-7} cm/sec after 18.4 pore volumes of cupric sulfate flow.

When the two curves are compared, it is clear that sample AC-23 had a greater increase and a higher end permeability than AC-22. The probable reason for this was that sample AC-22 was on cupric sulfate for only 2.1 pore

(a) AC-22



(b) AC-23

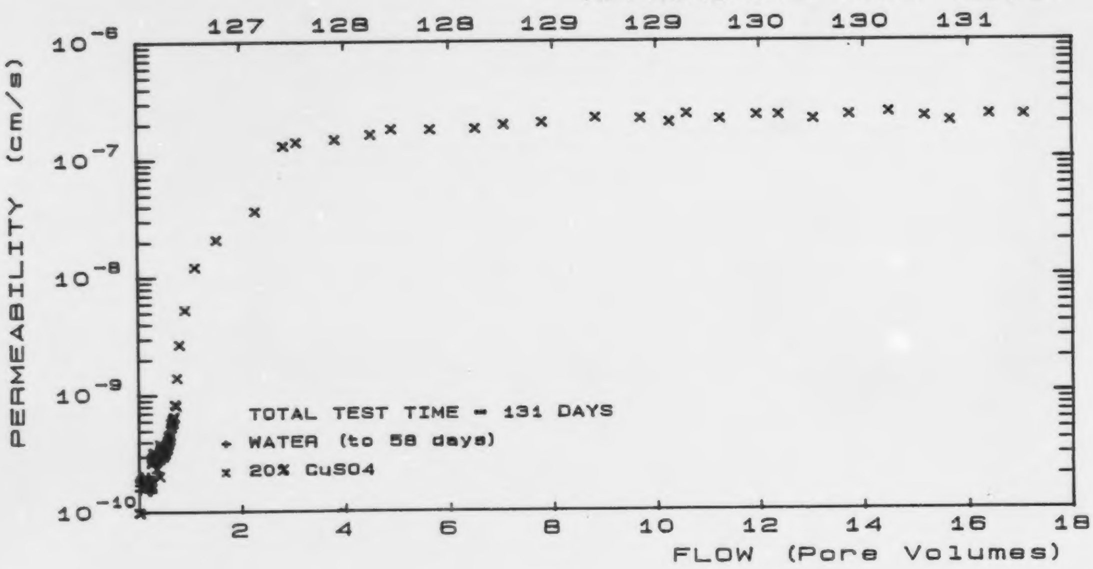


Figure 30. Permeability versus volume of flow of water and 20% cupric sulfate through acrylate grout. (a) Plot for sample AC-22. (b) Plot for sample AC-23.

volumes of flow, and was mistakenly terminated before its equilibrium permeability was reached. One may note that sample AC-23 had a permeability of approximately 3.7 x 10^{-8} cm/sec at a pore volume flow of 2.1 of cupric sulfate, close to the final permeability of sample AC-22, but with continued flow its permeability increased and finally equilibrated at 2.3 x 10^{-7} cm/sec.

- Acrylate Grout Samples Permeated With a 10% Solution of Cupric Sulfate - Phase III

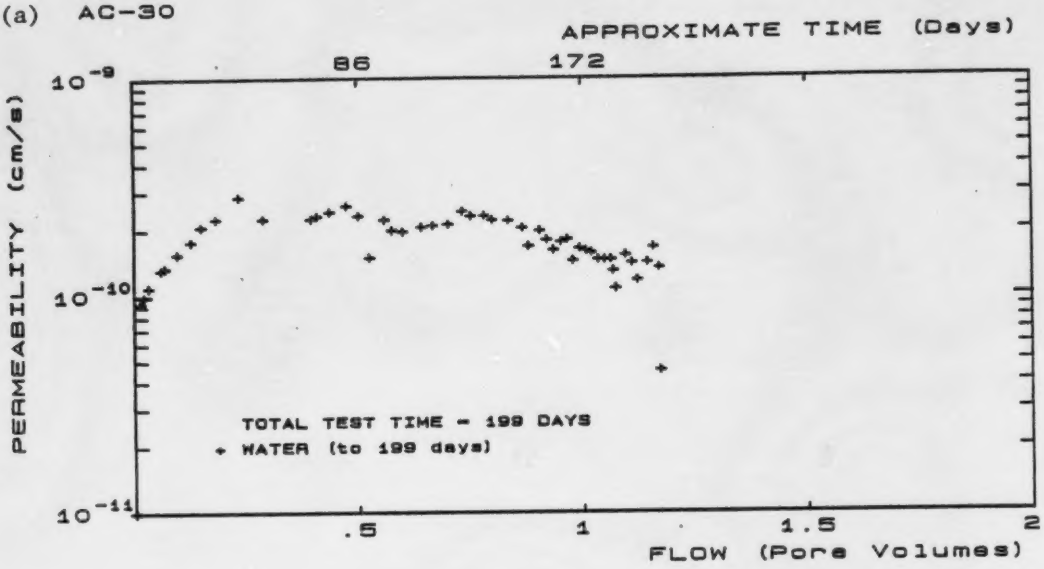
Two acrylate grout samples, designated AC-30 and AC-44, were tested with a 10% solution of cupric sulfate in water. Each sample had a diameter of 75 mm. Sample AC-30 had a thickness of 31 mm and AC-44 a thickness of 34 mm. Figures 31 and 32 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-30 was permeated with water for 199 days with an accumulated flow of 1.2 pore volumes. Sample AC-44 was tested on water for 44.1 days with an accumulated flow of 1.6 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi). Initially AC-30 was subjected to a backpressure of 69.0 kPa (10.0 psi) which was later reduced to zero. Sample AC-44 was tested at a constant backpressure of zero. The gradients varied somewhat due to the difference in sample thicknesses. Sample AC-30 had a gradient of 567 and AC-44 a gradient of 517. The plots of permeability versus flow show a fourfold variation between the two samples. The curve for AC-30 indicates an equilibrium permeability of 1.43 x 10^{-10} cm/sec as compared to 5.65 x 10^{-10} cm/sec for AC-44.

A 10% cupric sulfate solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the pressures and gradients were maintained at the same levels as had been used for testing with water. Sample AC-30 was permeated with chemical for 33.3 days with an accumulated chemical flow of 26.0 pore volumes. Sample AC-44 was permeated with the 10% cupric sulfate solution for 21.0 days with a sum chemical flow of 62.1 pore volumes.

After initial percolation of the 10% cupric sulfate solution, AC-30 demonstrated a very gradual increase in permeability that extended over a period of approximately ten days during which time nearly three pore volumes of the permeant was passed. Sample AC-30 came to an initial peak permeability of 1.4 x 10^{-8} cm/sec. By comparison, AC-44 exhibited a more abrupt change in permeability to an initial peak permeability of 4.4 x 10^{-8} cm/sec, slightly more than a threefold increase relative to AC-30. Following the first peak, AC-30 demonstrated a continued gradual increase in permeability until coming to a final equilibrium at 8.4 x 10^{-8} cm/sec. Sample AC-44, after its rapid initial increase in permeability, gradually came to an equilibrium of 1.1 x 10^{-6} cm/sec, while permeated at a very high gradient of 517. After a reduction of the gradient to 103, sample AC-44 underwent a decrease in permeability and came to a final equilibrium permeability of 1.0 x 10^{-7} cm/sec, a

(a) AC-30



(b) AC-30

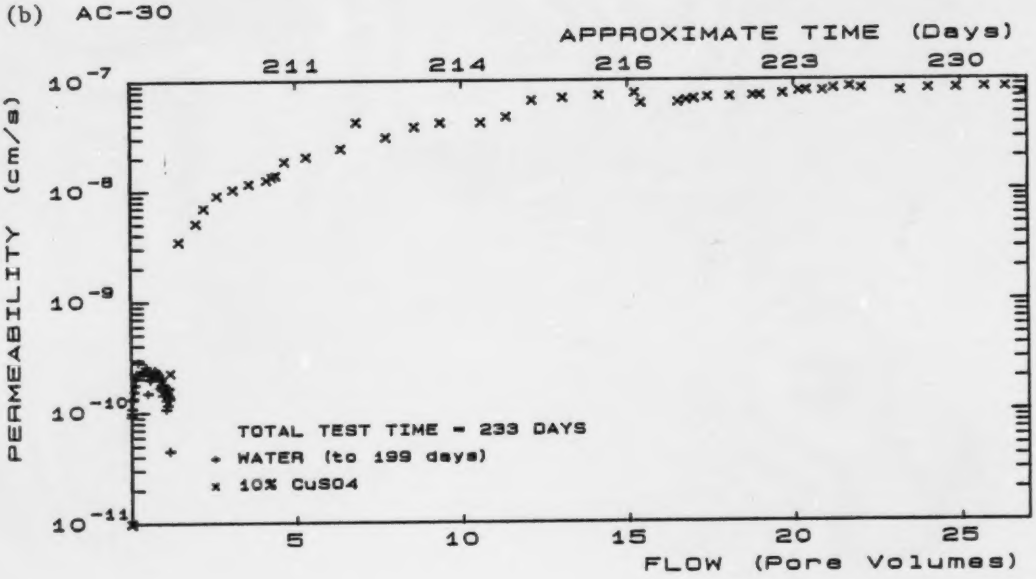


Figure 31. Permeability versus volume of flow through acrylate grout sample AC-30. (a) Water as permeant. (b) 10% cupric sulfate and water as permeants.

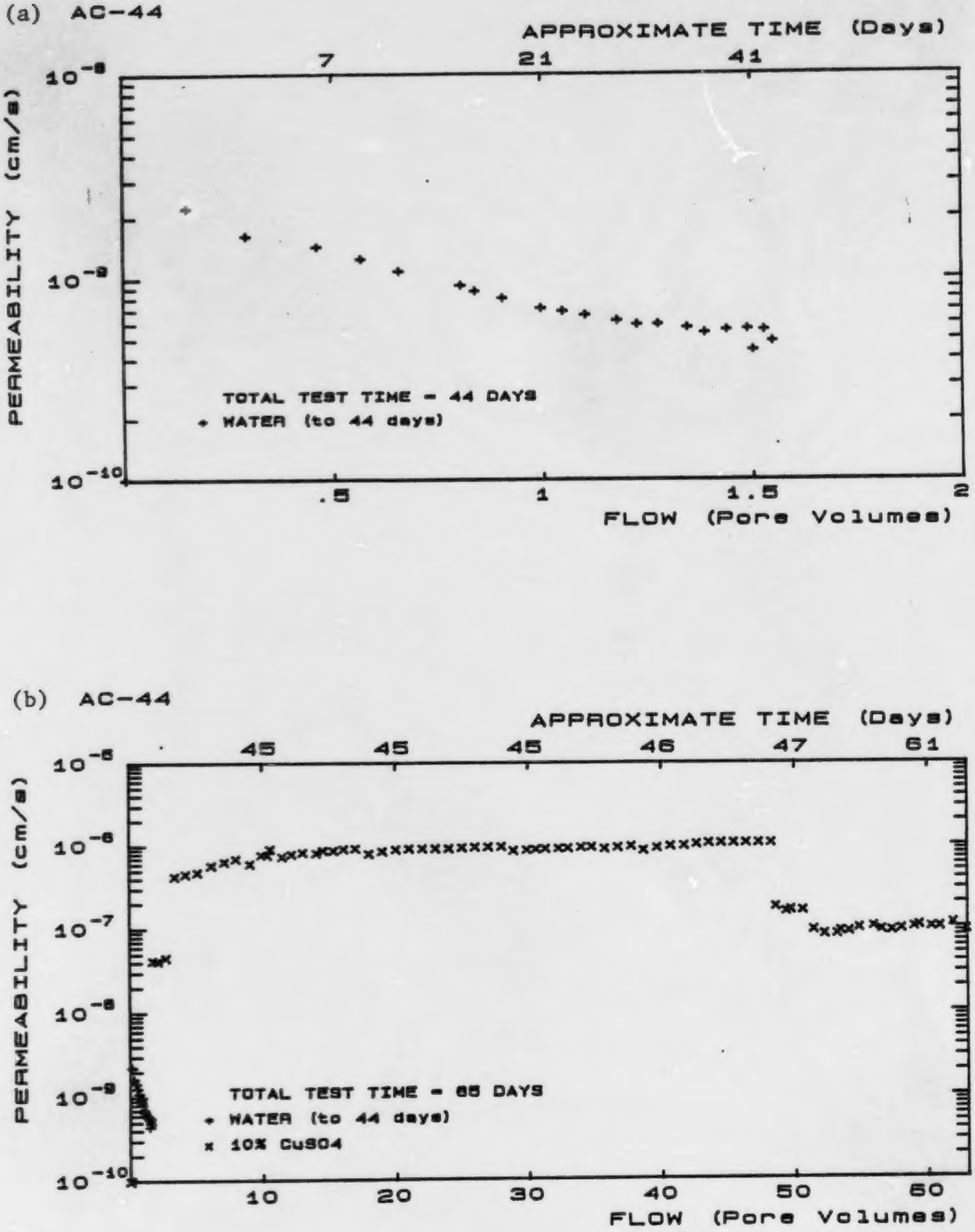


Figure 32. Permeability versus volume of flow through acrylate grout sample AC-44. (a) Water as permeant. (b) 10% cupric sulfate and water as permeants.

one order of magnitude decrease due to gradient effects. Tentatively, the conclusion may be drawn that a drop in gradient may have an effect on permeability when acrylate grout is permeated with a 10% solution of cupric sulfate in water.

These samples varied greatly in many respects except for their final equilibrium permeability values which were reached after the gradients were reduced to 114 for sample AC-30, and 103 for AC-44.

o Permeability Test of Acrylate Grout With 100% Ethylene Glycol

Two acrylate grout samples were tested with 100% ethylene glycol. They were designated as AC-1 and AC-11. The samples were 35 and 27 mm thick, respectively, and their diameter was 75 mm. Figure 33 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with water. Sample AC-1 was tested with water for 18 days with an accumulated flow of 0.2 pore volume, and sample AC-11 was permeated for 17 days and to a total flow of 0.7 pore volume with water. The test on AC-1 was conducted with a net confining pressure of 173 kPa (25 psi), a backpressure of 34.5 kPa (5 psi), and a gradient of 201. Sample AC-11 was tested with a net confining pressure of 155 kPa (22.5 psi), a backpressure of 69 kPa (10 psi), and a gradient of 651. The permeability versus flow curves of these samples show little variation; both curves are level and indicate an equilibrium permeability of between 7.2 and 6.5×10^{-10} cm/sec.

One hundred percent ethylene glycol was used as the chemical leachate in this test series. At the time of its introduction into sample AC-1 the backpressure on the sample was reduced to zero, and the net confining pressure was reduced to 121 kPa (17.5 psi). The gradient was increased to 271. With the introduction of the chemical, the permeability versus pore volume flow curve briefly turned lower, then proceeded to rise rapidly. With 0.16 pore volume of flow the sample reached a peak permeability of 2.2×10^{-7} cm/sec, which was followed by a slight reduction in its permeability to an equilibrium value of 1.5×10^{-7} cm/sec after only 0.3 pore volume of ethylene glycol flow. The test was continued for a total flow of 2.3 pore volumes of ethylene glycol, or a net testing time of 5 days, without any noticeable change in permeability. This final phase of testing on the chemical was conducted intermittently over a period of 30 days with short one-to-two hour test periods at high rates of flow, and with one to three day rest periods in between.

The 100% ethylene glycol was introduced into sample AC-11 with a gradient of 351 and zero backpressure. The effective confining pressure was reduced from the 155 kPa (22.5 psi) used with water to 121 kPa (17.5 psi) with ethylene glycol. The chemical caused a 0.4 order of magnitude immediate reduction in the permeability of the sample, which was followed by a gradual increase in permeability. The rise of the permeability versus flow curve occurred over a range of 1.5 pore volumes of ethylene glycol flow, and took 24 days. At that time the permeability of the sample reached a peak value of 1.9×10^{-8} cm/sec. This, upon continuing permeation, gradually decreased to a final

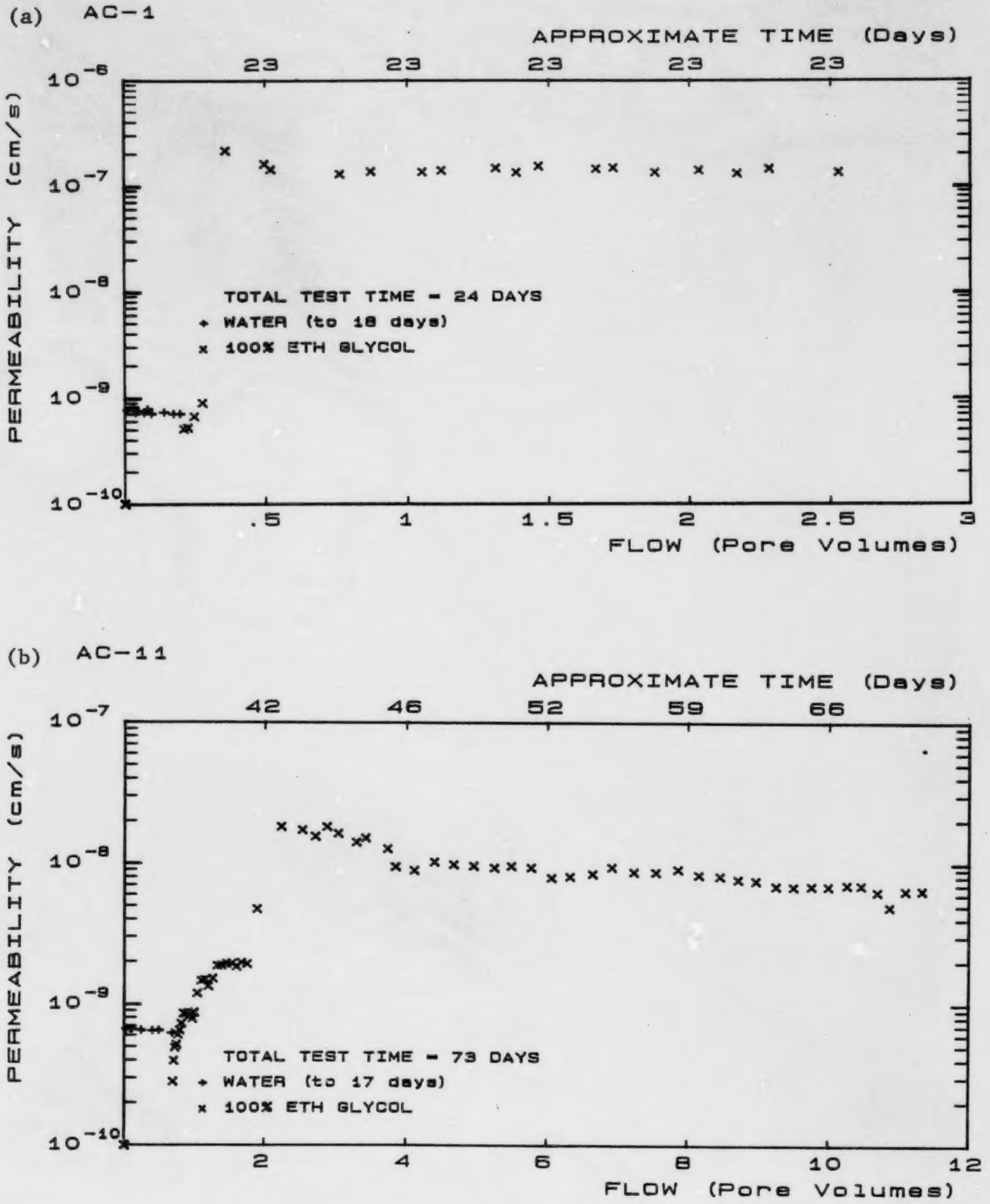


Figure 33. Permeability versus volume of flow of water and 100% ethylene glycol through acrylate grout. (a) Plot for sample AC-1. (b) Plot for sample AC-11.

equilibrium permeability of approximately 7.1 x 10^{-9} cm/sec, after a total flow of 8.6 pore volumes and 47 days with ethylene glycol.

The two acrylate samples gave different equilibrium permeability values with ethylene glycol. This may be attributed to the use of different confining pressures and gradients. Also, sample AC-1 was the first acrylate sample made and was not mounted for permeation with strong chemicals. For a long time it was on the testing board permeating on and off with water without official records, until the need arose to use it for testing with ethylene glycol. As a result, the sample was actually permeated with water for many more pore volumes than was recorded on its data sheets. This may have caused excessive leaching of sample AC-1 and a greater increase in its permeability with ethylene glycol than that of sample AC-11.

o Permeability Test of Acrylate Grout With 4N Hydrochloric Acid

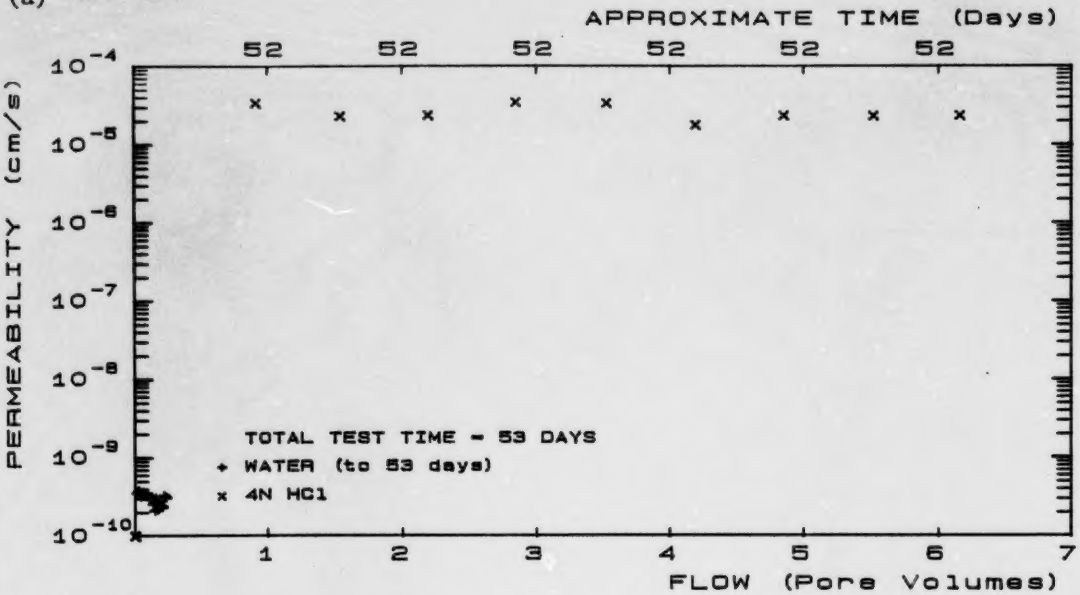
Two acrylate grout samples, AC-24 and AC-28, were tested with 4N hydrochloric acid. Their thicknesses were 43 and 31 mm, respectively, and both were 75 mm in diameter. Figure 34 shows the permeability test plots for the two samples.

Preceding the introduction of 4N hydrochloric acid, the two samples were saturated with water. The water permeation of both samples was accomplished at a net confining pressure of 121 kPa (17.5 psi), and with a headpressure of 173 kPa (25 psi) and a backpressure of 69 kPa (10 psi). Sample AC-24 was tested at a gradient of 245 for 73 days and to 0.24 pore volume of water flow, while sample AC-28 was permeated with water at a gradient of 340 for 36 days with an accumulated flow of 0.7 pore volume. The permeability of sample AC-24 equilibrated at 3.7 x 10^{-10} cm/sec. For sample AC-28 equilibrium occurred at 8.4 x 10^{-10} cm/sec.

The 4N hydrochloric acid was introduced into the samples at a headpressure of 104 kPa (15 psi), a tailpressure of 0, and a net confining pressure of 121 kPa (17.5 psi). The gradients for the two samples were maintained at 245 and 340, respectively. After the introduction of 4N hydrochloric acid, the permeabilities of both samples started to rise immediately. The initial portion of the permeability versus flow curve for sample AC-24 was very steep. This sample reached its first peak of permeability of 3.5 x 10^{-5} cm/sec within a few minutes of flow, and reached an equilibrium permeability of 2.4 x 10^{-5} cm/sec after only 1.3 pore volumes of flow of hydrochloric acid. Sample AC-28 behaved somewhat differently. Its permeability also started to rise immediately after the introduction of hydrochloric acid, but the rate of rise was slower. The sample reached its first peak of permeability of 4.3 x 10^{-7} cm/sec after 2.1 pore volumes of hydrochloric acid flow. From there it continued to rise slowly to a final equilibrium of 6.4 x 10^{-7} cm/sec. Testing of both samples was continued to an accumulated flow of 6.5 pore volumes of hydrochloric acid, and both test plots terminated in level segments.

When the two curves are compared, it is clear that sample AC-24 had a greater increase in permeability and a higher end permeability than sample AC-28. The reasons for this are not certain, but it may have been caused by

(a) AC-24



(b) AC-28

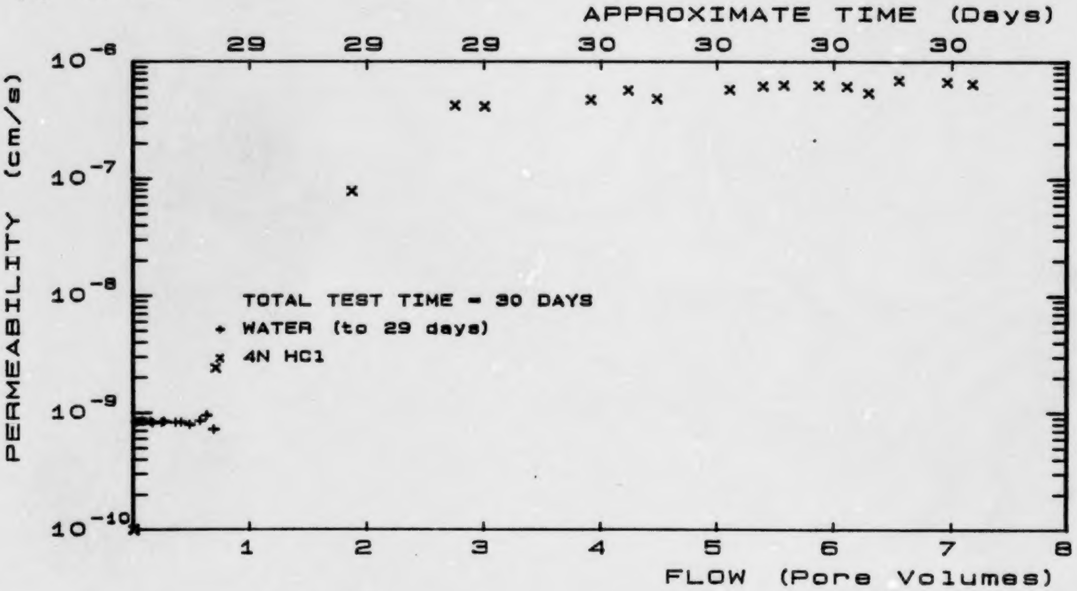


Figure 34. Permeability versus volume of flow of water and 4N hydrochloric acid through acrylate grout. (a) Plot for sample AC-24. (b) Plot for sample AC-28.

the incomplete water saturation of sample AC-24. Namely, this sample had only 0.24 pore volume of flow with water, as compared to the 0.7 pore volume for sample AC-28, before the introduction of hydrochloric acid.

- Acrylate Grout Samples Permeated With a 1N Solution of Hydrochloric Acid - Phase III

Two acrylate grout samples, designated AC-38 and AC-39, were tested with a 1N solution of hydrochloric acid in water. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 35 and 36 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-38 was permeated with water for 48.3 days with an accumulated flow of 1.9 pore volumes. Sample AC-39 was tested on water for 117 days with an accumulated flow of 3.0 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a gradient of 517. The backpressure for AC-38 was 69.0 kPa (10.0 psi) as opposed to zero for AC-39. The water permeability versus pore volume flow curves for AC-38 and AC-39 show little variation in comparison to one another. The curve for AC-38 indicates an equilibrium permeability of 7.8 x 10^{-10} cm/sec as compared to 5.9 x 10^{-10} cm/sec for AC-39.

A 1N hydrochloric acid solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi). The backpressure was decreased to zero for AC-38 and maintained at zero for AC-39. The gradient remained at 517. Sample AC-38 was permeated with chemical for 0.75 day with an accumulated chemical flow of 55.6 pore volumes. Sample AC-39 was permeated with the 1N hydrochloric acid solution for 3.0 days with a sum chemical flow of 68.9 pore volumes. The initial permeability plateau for each sample was reached almost instantaneously. The permeabilities were quite similar in magnitude: 4.0 x 10^{-6} cm/sec for AC-38 and 2.7 x 10^{-6} cm/sec for AC-39. Beyond that, due to their high permeability, the samples were tested with intermittent percolation periods with varying rest periods in between, generally one to seven days. There was a behavioral difference between the samples in their chemical leachate/grouted soil reaction after their initial permeability plateau was reached. AC-39 never varied greatly from its initial plateau. A total of fifteen percolation periods with varying rest periods in between extended over thirty-five days. The last nine periods were tested at a reduced gradient of 103, and at unchanged backpressure and net confining pressure of zero and 120.8 kPa (17.5 psi), respectively. This gradient reduction induced a very slight decrease in permeability to a new equilibrium of 1.5 x 10^{-6} cm/sec. In contrast, AC-38 demonstrated a stair-step nature in its permeability versus pore volume relationship. Final equilibrium permeability was assumed to occur when two separate percolation periods yielded similar permeability magnitudes. Three percolation periods were tested at a gradient of 517 and three at a gradient of 103. In both instances the net confining pressure and backpressure remained unchanged at 120.8 kPa (17.5 psi) and zero, in the stated order. For the former gradient an equilibrium permeability of 1.9 x 10^{-5} cm/sec was obtained as opposed to a slightly

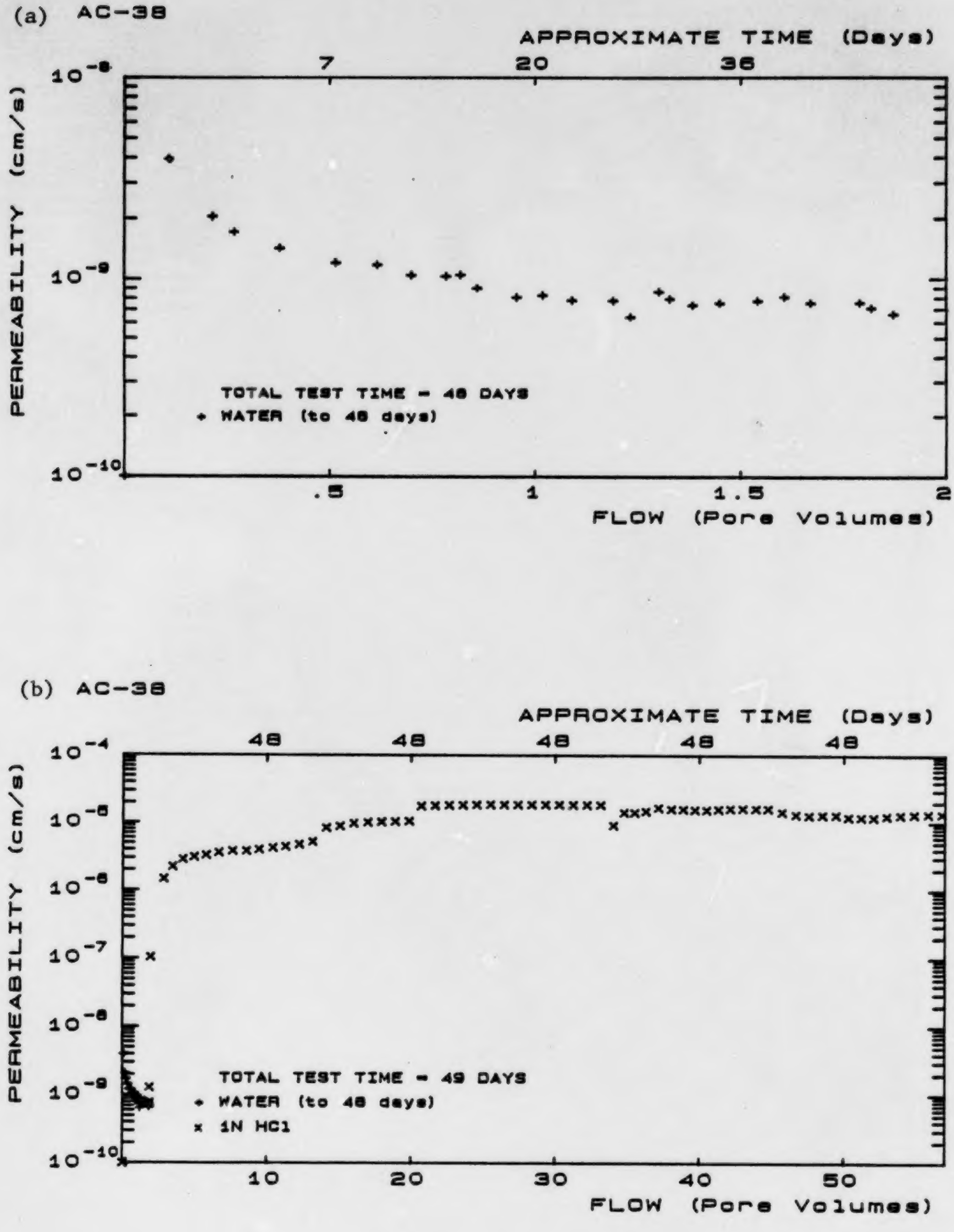


Figure 35. Permeability versus volume of flow through acrylate grout sample AC-38. (a) Water as permeant. (b) Water and 1N hydrochloric acid as permeants.

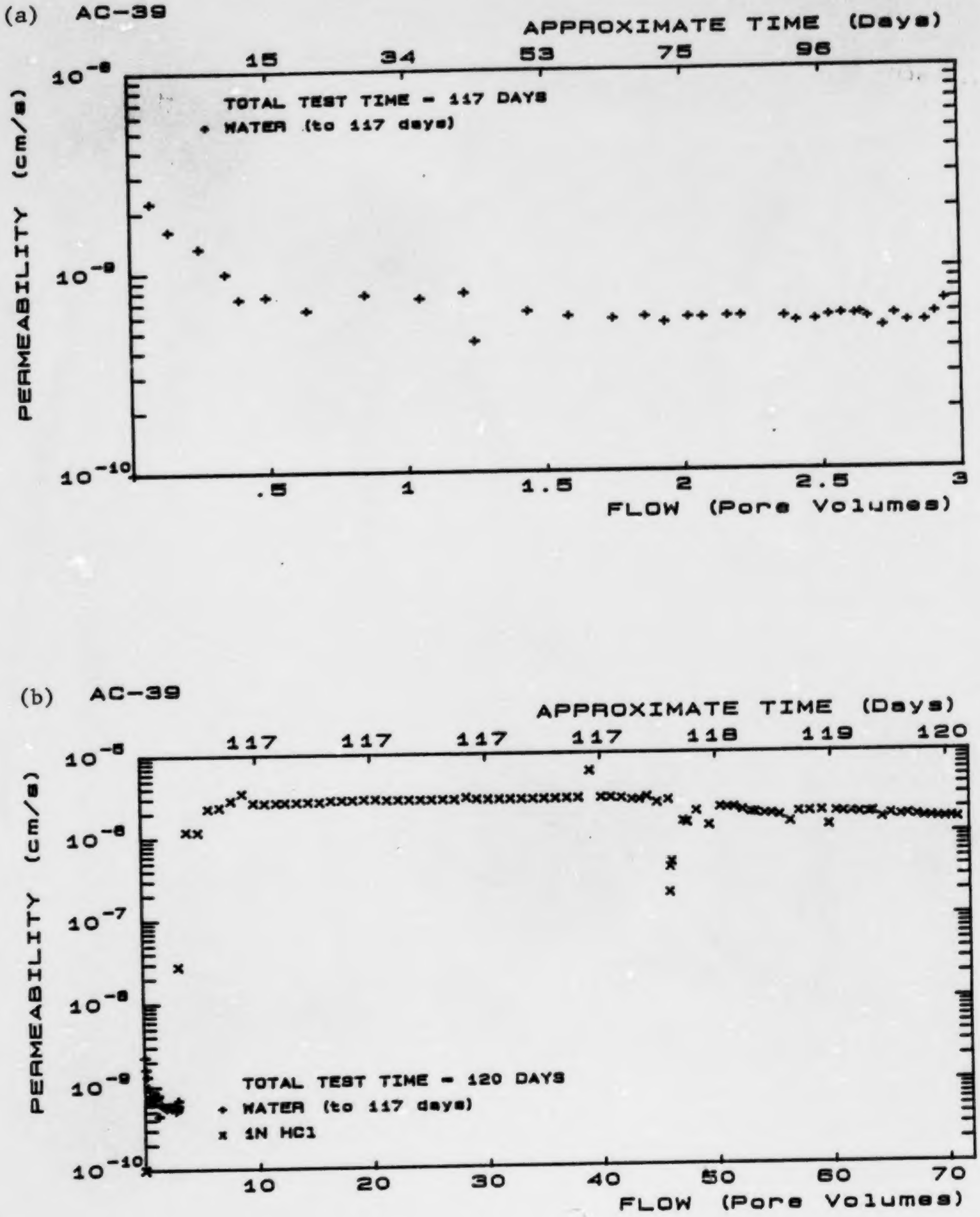


Figure 36. Permeability versus volume of flow through acrylate grout sample AC-39. (a) Water as permeant. (b) Water and 1N hydrochloric acid as permeants.

lower permeability of 1.4 x 10^{-5} cm/sec for the reduced gradient. Compared to AC-39, these permeabilities were larger by approximately one order of magnitude.

o Permeability Test of Acrylate Grout With 100% Methanol

In Phase II of this project, three acrylate samples were tested with 100% methanol. The sample designations were AC-7, AC-10, and AC-12. The samples had thicknesses of 38, 42 and 33 mm, respectively. The diameter of each of the three samples was 75 mm. Figures 37 and 38 show the permeability versus pore volume flow curves for these samples.

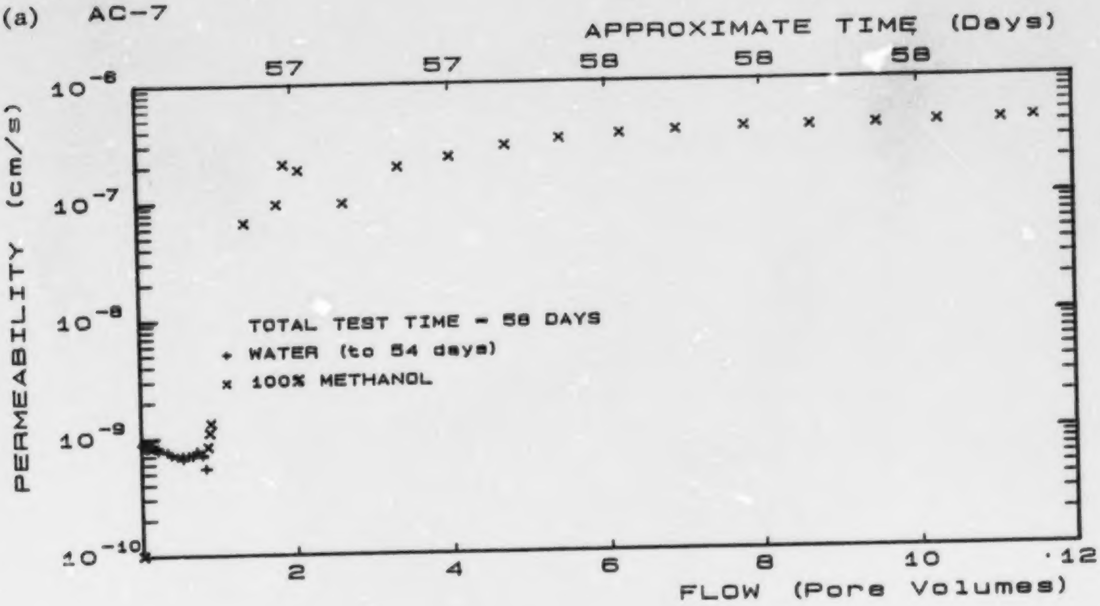
The above samples were saturated with water under the following test conditions. Sample AC-7 was tested with water using a headpressure that was initially set at 104 kPa (15 psi) and was later increased to 173 kPa (25 psi). The tailpressure was maintained throughout the test at 34.5 kPa (5 psi). The effective confining pressure changed from a starting 173 kPa (25 psi) to 138 kPa (20 psi) with the change in headpressure. The gradient at the beginning of the test was 185 and was later increased to 278 and then to 370. Sample AC-10 was tested with water at a headpressure that was first set at 173 kPa (25 psi) and was later increased to 242 kPa (35 psi), and at a tailpressure which was first set to 34.5 kPa (5 psi) and was increased to 69 kPa (10 psi) toward the end of its test with water. The effective confining pressure was 138 kPa (20 psi) at the beginning but was increased to 155 kPa (22.5 psi) in the later stages of the test. The gradient at first was 335 and was later increased to 419. Sample AC-12 was permeated with water at a headpressure of 242 kPa (35 psi), a tailpressure of 69 kPa (10 psi), an effective confining pressure of 155 kPa (22.5 psi), and a gradient of 533.

The equilibrium permeabilities, total flow in pore volumes and duration of tests with water were as follows: 7.2 x 10^{-10} cm/sec, 0.99 pore volume and 63 days for sample AC-7; 2.6 x 10^{-10} cm/sec, 0.33 pore volume and 56 days for sample AC-10; and 7.0 x 10^{-10} cm/sec, 0.58 pore volume and 20 days for sample AC-12. All three samples exhibited stable equilibrium permeabilities with water.

The introduction of 100% methanol was achieved under the following pressure conditions. Sample AC-7 was tested with methanol under a headpressure of 138 kPa (20 psi), a tailpressure of 0, a net confining pressure of 173 kPa (25 psi), and a gradient of 370. Sample AC-10 was permeated with a headpressure of 104 kPa (15 psi), a tailpressure of 0, and an effective confining pressure of 190 kPa (27.5 psi) at the beginning of the test. The confining pressure was later reduced to 121 kPa (17.5 psi). A gradient of 251 was used. Sample AC-12 was tested on methanol at a headpressure of 104 kPa (15 psi), a tailpressure of 0, an effective confining pressure of 121 kPa (17.5 psi) and a gradient of 320.

The introduction of methanol caused an immediate sharp increase in the permeabilities of all three samples. Sample AC-7 underwent a jump of more than two orders of magnitude in its permeability to a level of 9.2 x 10^{-8} cm/sec in only three days and with only 0.96 pore volume flow of methanol. Beyond that, the permeability versus pore volume flow curve continued to rise

(a) AC-7



(b) AC-10

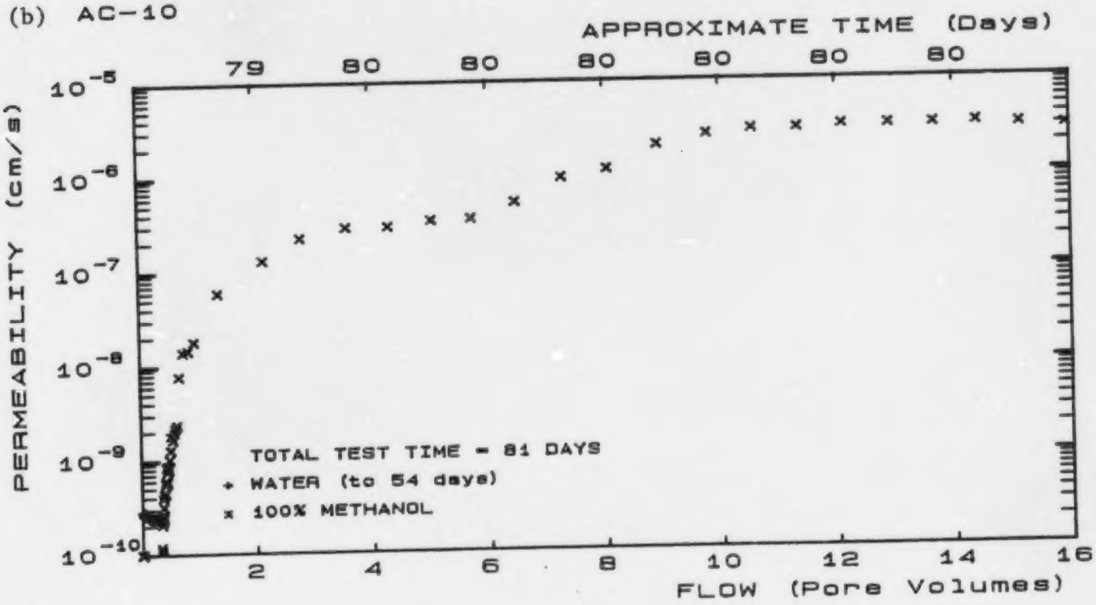


Figure 37. Permeability versus volume of flow of water and 100% methanol through acrylate grout. (a) Plot for sample AC-7. (b) Plot for sample AC-10.

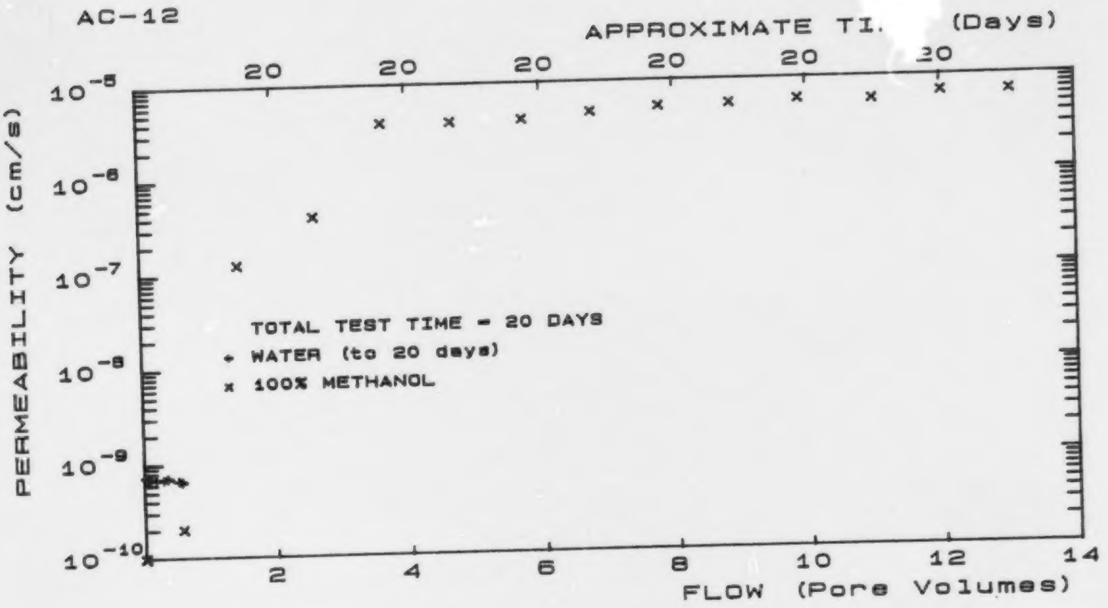


Figure 38. Permeability versus volume of flow of water and 100% methanol through acrylate grout sample AC-12.

more slowly until the sample reached a final equilibrium permeability of 4.2 x 10^{-7} cm/sec, after a flow of 10.7 pore volumes of methanol.

The permeation of 100% methanol through sample AC-10 caused an immediate increase in the permeability of the sample. The permeability versus pore volume flow curve first rose sharply, then tapered off. After 34 days and 3.3 pore volumes of flow of methanol, the curve leveled off at a permeability of 3 x 10^{-7} cm/sec. Following this period there was an increase in the permeability of the sample, and after a total flow of 11.8 pore volumes of methanol, the sample came to an equilibrium at a permeability of 3.2 x 10^{-6} cm/sec. This permeability was maintained until the end of the test after a total flow of 15.7 pore volumes of methanol.

The introduction of methanol into sample AC-12 first caused a slight decrease in its permeability, then approximately two orders of magnitude increase after 5 days of testing and 3.1 pore volumes of flow of methanol. The sample permeability reached 4.0 x 10^{-6} cm/sec. This was followed by a further sharp rise in permeability that ultimately resulted in an equilibrium permeability of 6.2 x 10^{-6} cm/sec, after a total of 12.5 pore volumes of flow of methanol.

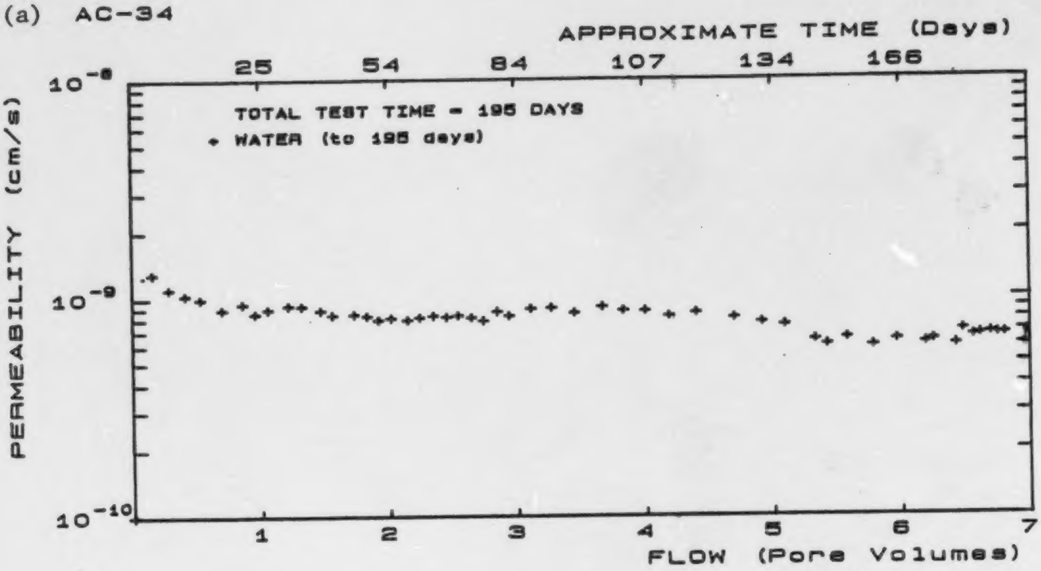
As can be seen from the three permeability versus flow plots, these samples behaved quite similarly, namely, after an initial sharp rise, their permeability flow curves all came to a level equilibrium value of permeability. Each sample had a methanol flow that exceeded 10 pore volumes. It can be observed that the final equilibrium permeability of sample AC-7 was approximately 1 order of magnitude lower than that of samples AC-10 and AC-12. The reason for this may have been that sample AC-7 was permeated with water for a total pore volume flow that was twice as much as that for either sample AC-10 or sample AC-12. Thus, it may be assumed that at the time of the introduction of methanol, AC-7 was more highly saturated than the other two samples. However, when the test results for these three samples are compared to the results obtained in Phase III for samples AC-34 and AC-45, there are great discrepancies in their final equilibrium permeabilities. Presently, there seems to be no explanation for this difference.

- Acrylate Grout Samples Permeated With 100% Methanol - Phase III

Two acrylate grout samples, designated AC-34 and AC-45, were tested with 100% methanol. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 39 and 40 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-34 was permeated with water for 195 days with an accumulated flow of 6.9 pore volumes. Sample AC-45 was tested on water for 25.8 days with an accumulated flow of 0.8 pore volume. The testing was conducted with a net confining pressure of 241.5 and 120.8 kPa (35.0 and 17.5 psi) for AC-34 and AC-45, respectively; a backpressure of 69.0 kPa (10.0 psi); and a gradient of 517. The water permeability versus pore volume flow curves for AC-34

(a)



(b)

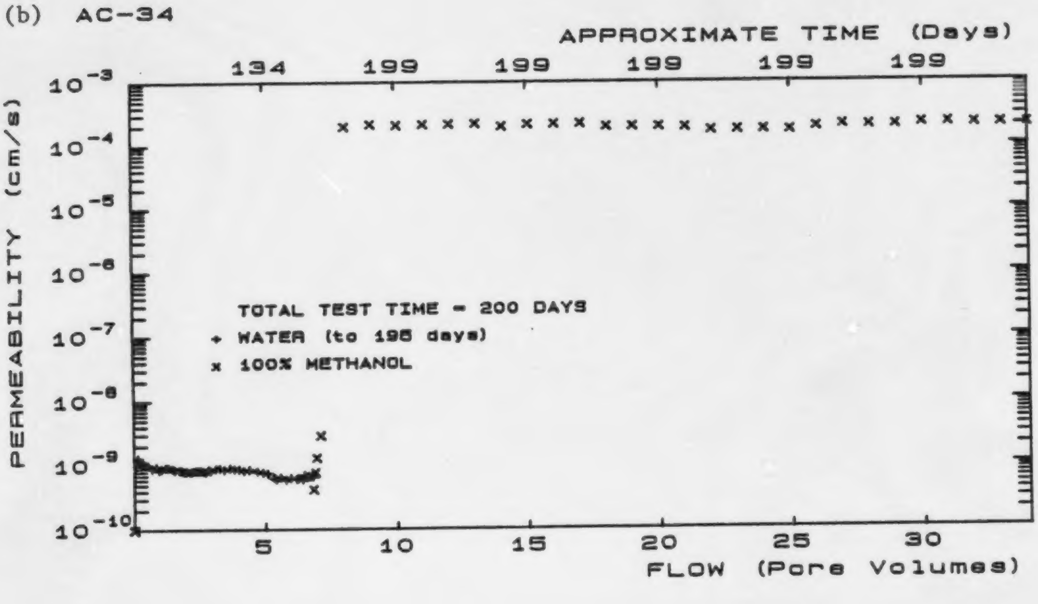
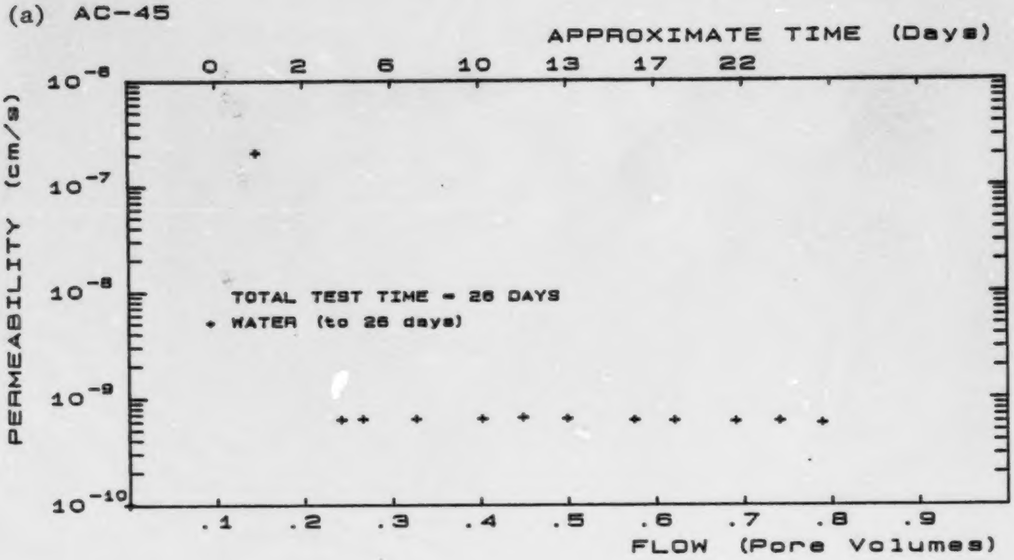


Figure 39. Permeability versus volume of flow through acrylate grout sample AC-34. (a) Water as permeant. (b) Water and 100% methanol as permeants.

(a) AC-45



(b) AC-45

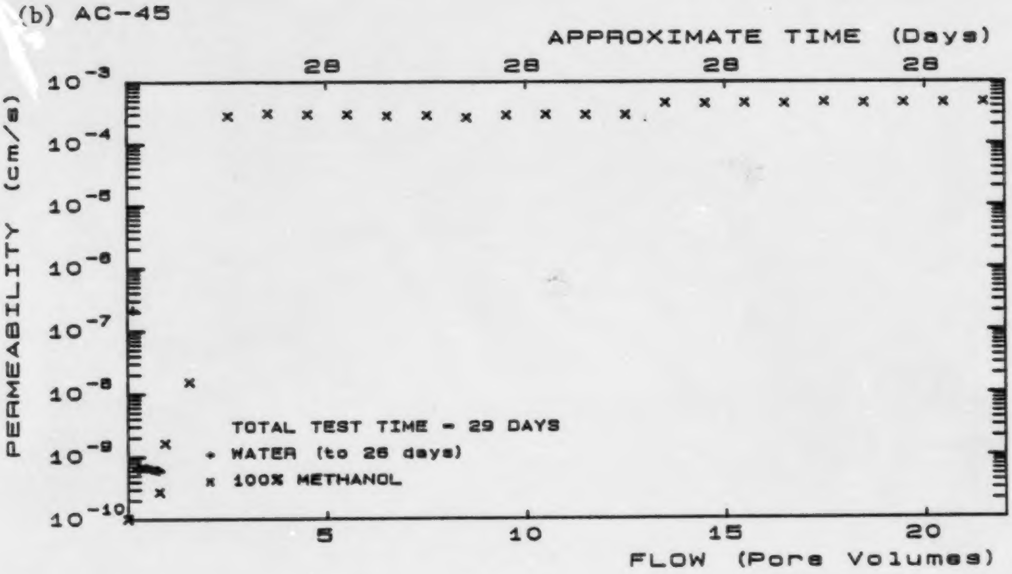


Figure 40. Permeability versus volume of flow through acrylate grout sample AC-45. (a) Water as permeant. (b) Water and 100% methanol as permeants.

and AC-45 show little variation compared to one another. The curve for AC-34 indicates an equilibrium permeability of 6.6×10^{-10} cm/sec, as compared to 6.4×10^{-10} cm/sec for AC-45.

Reagent grade methanol was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure and gradient were set at the levels used in the tests on water, however, the backpressure was decreased to zero. Sample AC-34 was permeated with chemical for 4.2 days with an accumulated chemical flow of 27.5 pore volumes. Sample AC-45 was permeated with 100% methanol for 3.0 days with a sum chemical flow of 21.0 pore volumes. The two samples exhibited similar permeability behavior. A gradual loss of permeability took place over a period of three to four days, after which an abrupt increase of permeability was demonstrated.

Initial permeability plateaus were 2.2×10^{-4} cm/sec and 2.9×10^{-4} cm/sec for samples AC-34 and AC-45, respectively. Final equilibrium permeabilities did not change appreciably from these initial values even after a series of stops and restarts in the percolation process. Generally a rest period of one to seven days existed between the percolation periods. A total of four percolation periods with varying rest periods in between extended over approximately eight days for sample AC-45. The last two test periods were performed with a reduced gradient of 104, upon which the permeability increased slightly to 4.6×10^{-4} cm/sec. Sample AC-34 did not demonstrate an increase in permeability when its gradient was reduced to 104. In addition, it had one more percolation period which extended its testing time to fifteen days. Throughout this, its permeability remained at 2.1×10^{-4} cm/sec.

- Acrylate Grout Samples Permeated With a 25% Solution of Methanol - Phase III

Two acrylate grout samples, designated AC-27 and AC-29, were tested with a 25% solution of methanol in water. Each sample had a diameter of 75 mm. Sample AC-27 had a thickness of 35 mm, AC-29 a thickness of 32 mm. Figures 41 and 42 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample AC-27 was permeated with water for 245 days with an accumulated flow of 1.0 pore volume. Sample AC-29 was tested on water for 201 days with an accumulated flow of 4.1 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of 69.0 kPa (10.0 psi). The gradients varied due to differences in driving head and, to a small degree, due to the difference in sample thicknesses. Sample AC-27 had a gradient of 302, and AC-29 a gradient of 550. Sample AC-27 had an equilibrium permeability of 1.8×10^{-10} cm/sec, as compared to 6.3×10^{-10} cm/sec for AC-29.

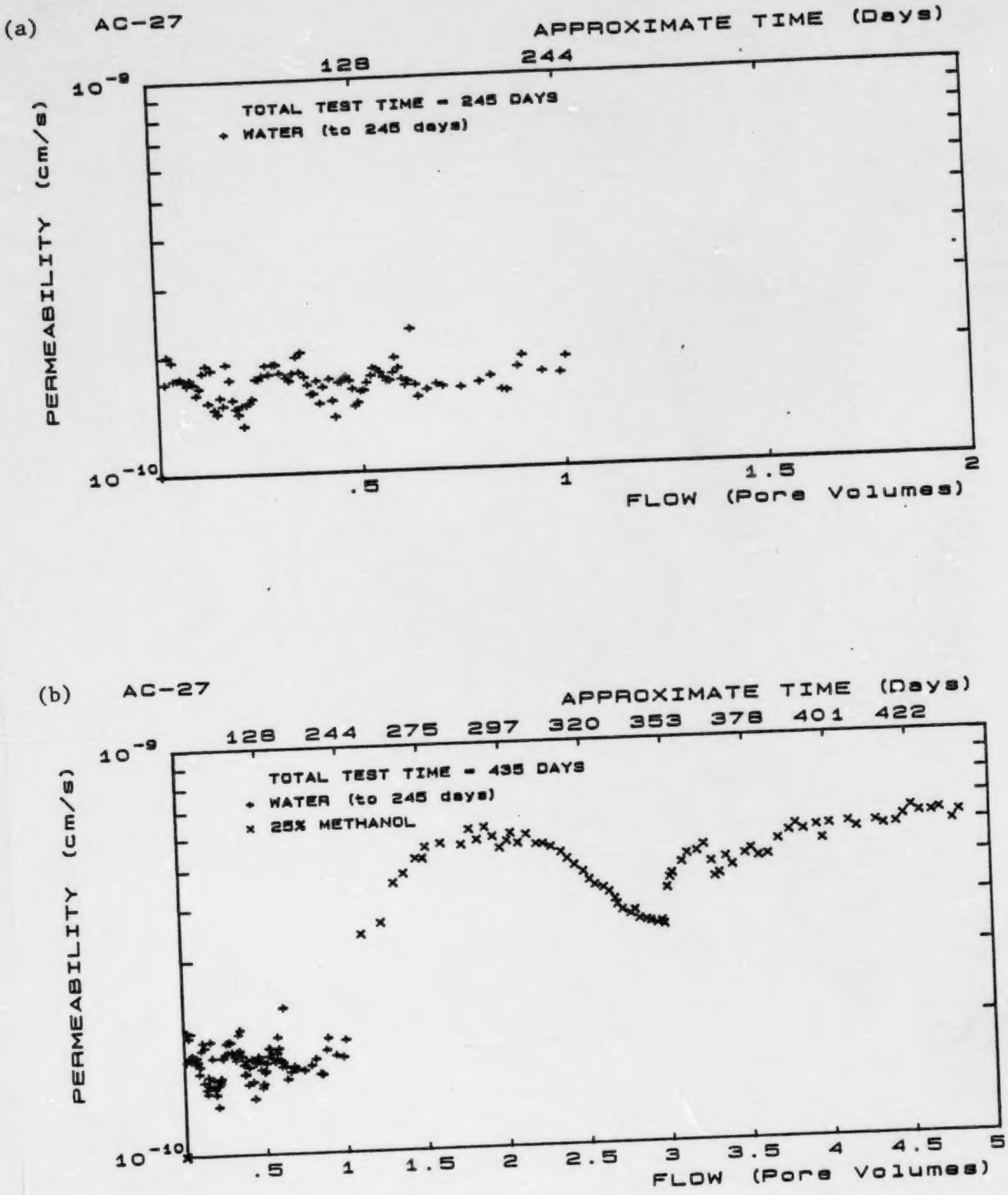
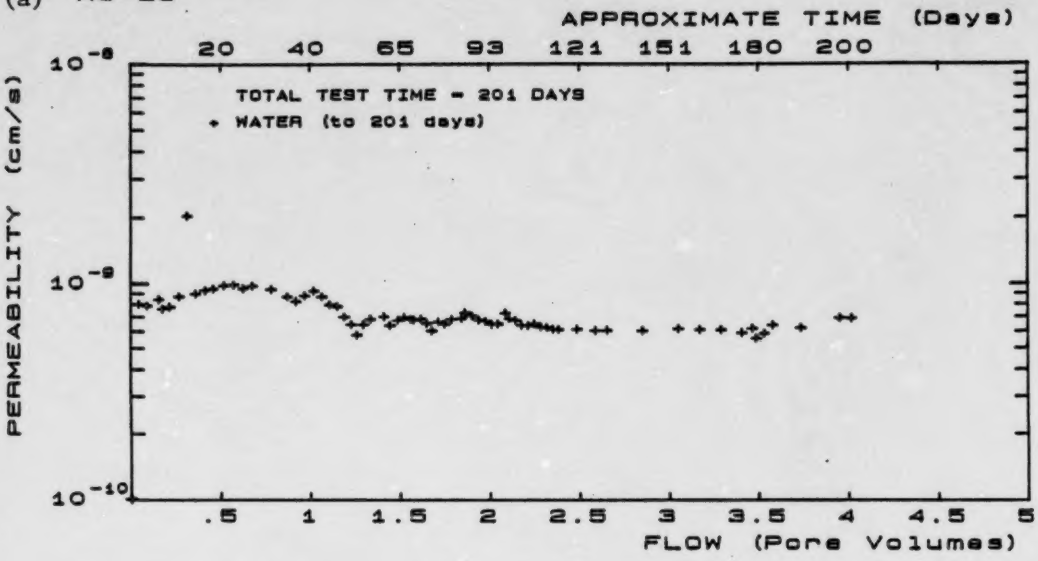


Figure 41. Permeability versus volume of flow through acrylate grout sample AC-27. (a) Water as permeant. (b) Water and 25% methanol as permeants.

(a) AC-29



(b) AC-29

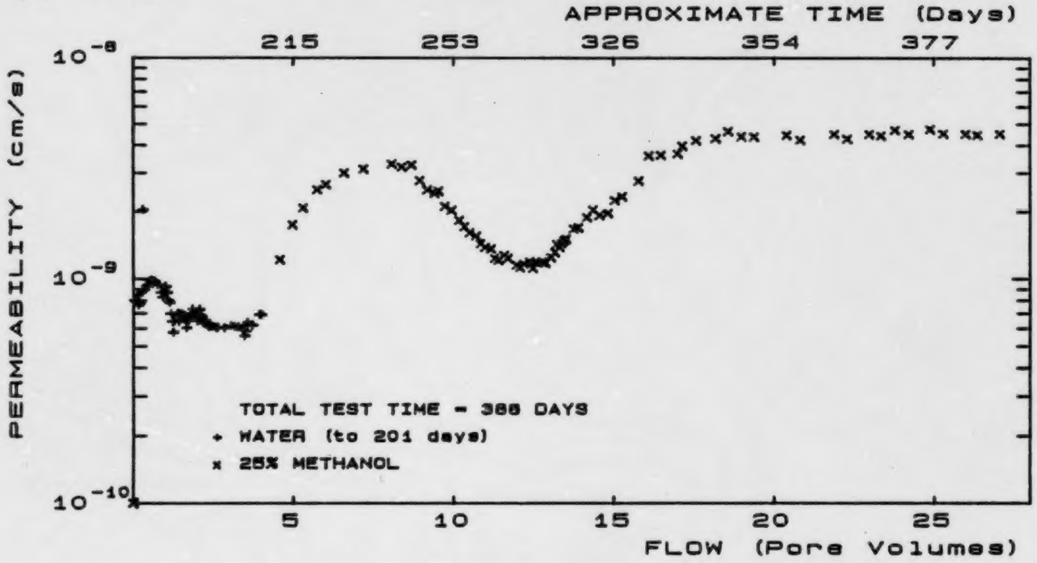


Figure 42. Permeability versus volume of flow through acrylate grout sample AC-29. (a) Water as permeant. (b) Water and 25% methanol as permeants.

A 25% methanol solution was used as the chemical leachate for this pair of samples. When the chemical was introduced into sample AC-29, the pressures and gradients were held at the levels used for the tests on water. For sample AC-27 the driving head and tail pressures were adjusted to increase the gradient to 503. Sample AC-27 was permeated with chemical for 190 days with an accumulated chemical flow of 3.9 pore volumes. Sample AC-29 was permeated with the 25% methanol solution for 187 days with a sum chemical flow of 23.3 pore volumes. Permeation time was essentially the same in each instance but due to differences in permeability the pore volume flow varied greatly. In spite of the nearly one order of magnitude variance in the final equilibrium permeabilities of 6.4 x 10^{-10} and 4.6 x 10^{-9} cm/sec for AC-27 and AC-29, respectively, the curves demonstrate a very similar shape.

Initially both curves behaved sinusoidally and after one and a half cycles came to a final equilibrium permeability. The first peak in each curve very nearly approximated the final equilibrium permeability. AC-27 first peaked at 6.3 x 10^{-10} cm/sec after 0.9 pore volume of chemical leachate had passed through the sample over the course of roughly 47 days. Comparatively, AC-29 peaked at 3.4 x 10^{-9} cm/sec after 4.1 pore volumes of the 25% methanol solution passed through the sample over a period of 38 days.

Differences in the final equilibrium permeabilities can be partially attributed to the fourfold variation in the water baseline permeabilities. The final equilibrium permeability of AC-27 was almost four times as great in relation to its baseline equilibrium permeability, whereas the final equilibrium permeability for AC-29 was slightly more than seven times as great in relation to its water baseline permeability.

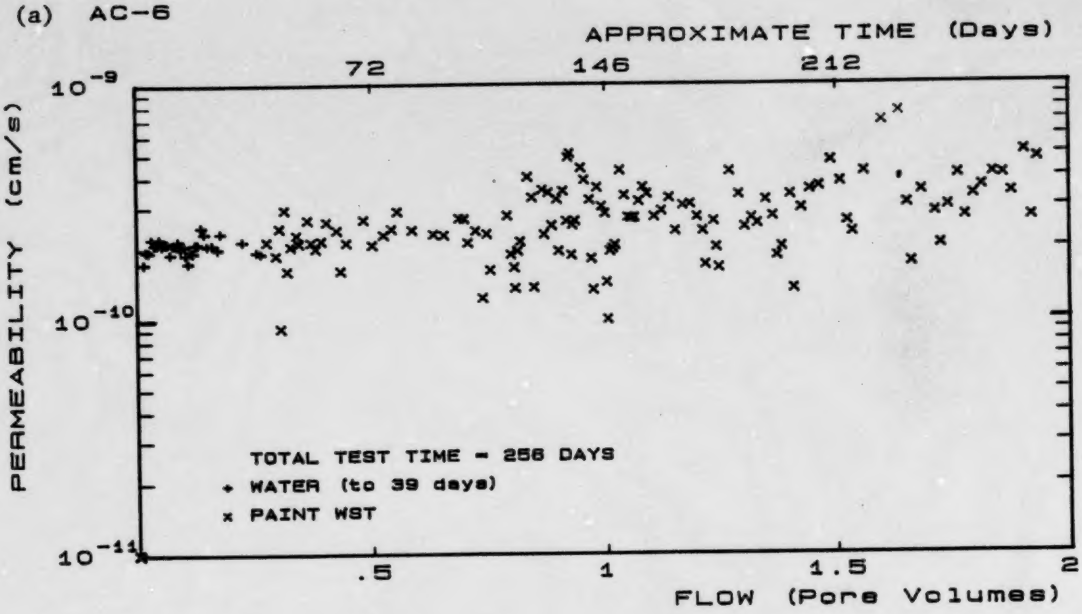
- Permeability Test of Acrylate Grout With Real-Site Paint Waste

The two acrylate samples tested on real-site paint waste were AC-6 and AC-19. They had a diameter of 75 mm and thicknesses of 37 and 33 mm, respectively. Figure 43 shows the permeability versus flow plots for the two samples.

The samples had the following equilibrium permeabilities with water: 2.2 x 10^{-10} cm/sec for sample AC-6, and 6.8 x 10^{-10} cm/sec for sample AC-19. The water was forced through sample AC-6 at a headpressure of 123 kPa (25 psi), a tailpressure of 34.5 kPa (5 psi), a net confining pressure of 138 kPa (20 psi), and a gradient of 380. The water was permeated through sample AC-19 with a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), a net confining pressure of 121 kPa (17.5 psi), and a gradient of 325.

The paint waste was introduced into sample AC-6 at a headpressure of 138 kPa (20 psi) and a tailpressure of zero. However, the headpressure was changed several times during the test, varying between 173 and 104 kPa (25 and 15 psi). Consequently, the net confining pressure varied too, and had values between 104 and 190 kPa (15 and 27.5 psi). The gradient also varied from a high of 475 to a low of 285. These changes explain the unusual scatter of the test points on the permeability versus pore volume flow plot. However, the average permeability of the sample did not

(a) AC-6



(b) AC-19

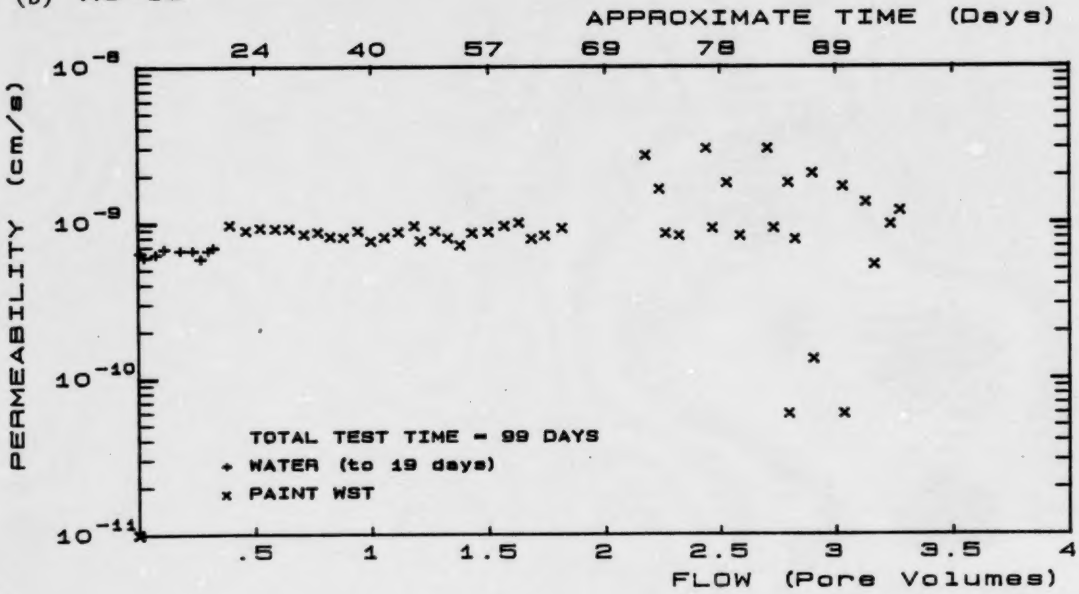


Figure 43. Permeability versus volume of flow of water and real-site paint waste through acrylate grout. (a) Plot for sample AC-6. (b) Plot for sample AC-19.

increase appreciably from that obtained on water. After 217 days and 1.67 pore volumes of flow of paint waste, the final permeability of the sample was still only 5 x 10^{-10} cm/sec.

With paint waste, sample AC-19 was first tested at a headpressure of 138 kPa (20 psi), which was later reduced to 104 kPa (15 psi). The tailpressure was maintained at 0 throughout the test. The net confining pressure was first set at 104 kPa (15 psi) and was later increased to 121 kPa (17.5 psi). The gradient was initially set at 433 and later in the test reduced to 325. Again, there was some scatter of test points on the plot; however, the final permeability was estimated to be approximately 1.0 x 10^{-9} cm/sec after 80 days and nearly 3 pore volumes of flow of paint waste.

As can be seen, the real-site paint waste had relatively little effect on the permeability of acrylate grout samples.

- Permeability Test of Acrylate Grout With Real-Site Refinery Waste

The two acrylate samples tested with real-site refinery waste were AC-5 and AC-13. Their diameter was 75 mm, and their thicknesses were 40 and 31 mm, respectively. Figure 44 shows the permeability versus flow plots for the two samples.

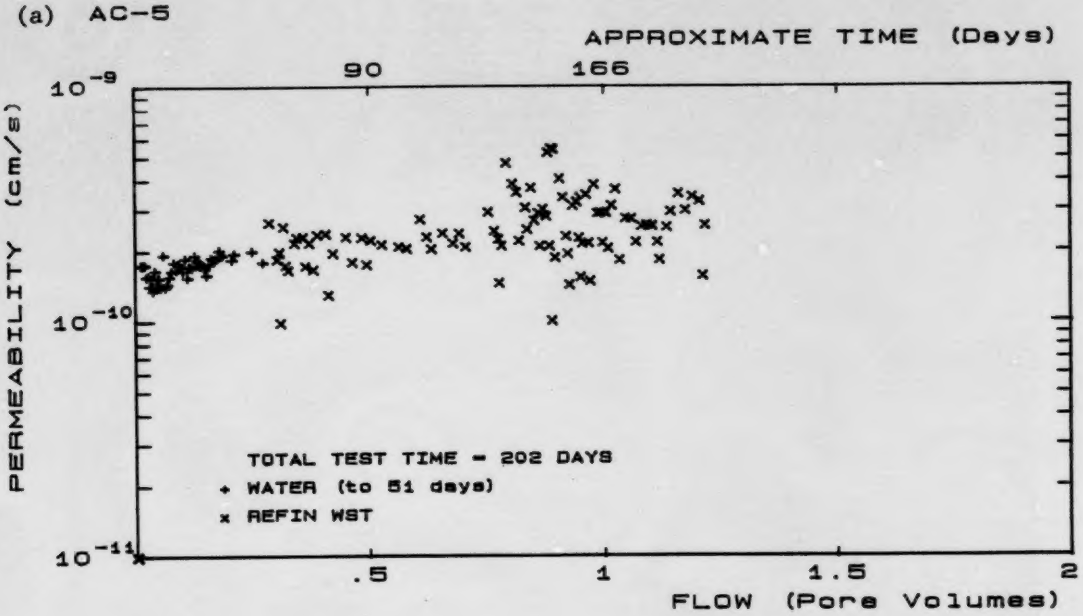
Sample AC-5 was saturated with water under varying pressure conditions. The headpressure varied between 173 and 276 kPa (25 and 40 psi), the tailpressure between 34.5 and 0 kPa (5 and 0 psi), and the net confining pressure between 138 and 173 kPa (20 and 25 psi). Consequently, the gradient of flow varied between 352 and 704. The equilibrium permeability of this sample with water was approximately 2 x 10^{-10} cm/sec, after 0.27 pore volume of water flow and 53 days.

The real-site refinery waste was introduced into sample AC-5 at a headpressure of 138 kPa (20 psi), which was later increased to 173 kPa (25 psi) and finally reduced to 69 kPa (10 psi). The tailpressure was 0 throughout the test. The net confining pressure varied between 104 and 173 kPa (15 and 25 psi). The gradient varied from 352 to 440. Upon the introduction of the refinery waste, there was an approximately 0.1 order of magnitude increase in the permeability of the sample. Even though the data points are scattered on the graph, there seems to be little further change in permeability. The final equilibrium permeability was approximately 2.8 x 10^{-10} cm/sec after 149 days and 0.95 pore volume of flow of refinery waste.

Sample AC-13 was permeated with water using the following pressures: a headpressure of 242 kPa (35 psi), a tailpressure of 69 kPa (10 psi), a net confining pressure of 155 kPa (22.5 psi), and a gradient of 568. Its equilibrium permeability with water was 7.6 x 10^{-10} cm/sec.

The refinery waste was introduced into sample AC-13 with a headpressure of 138 kPa (20 psi), a tailpressure of 0, a net confining pressure of 104 kPa (15 psi), and a gradient of 454. For twelve days during the middle of the test, the headpressure was temporarily dropped to 104 kPa (15 psi) and thereby the gradient lowered to 341. The introduction of

(a) AC-5



(b) AC-13

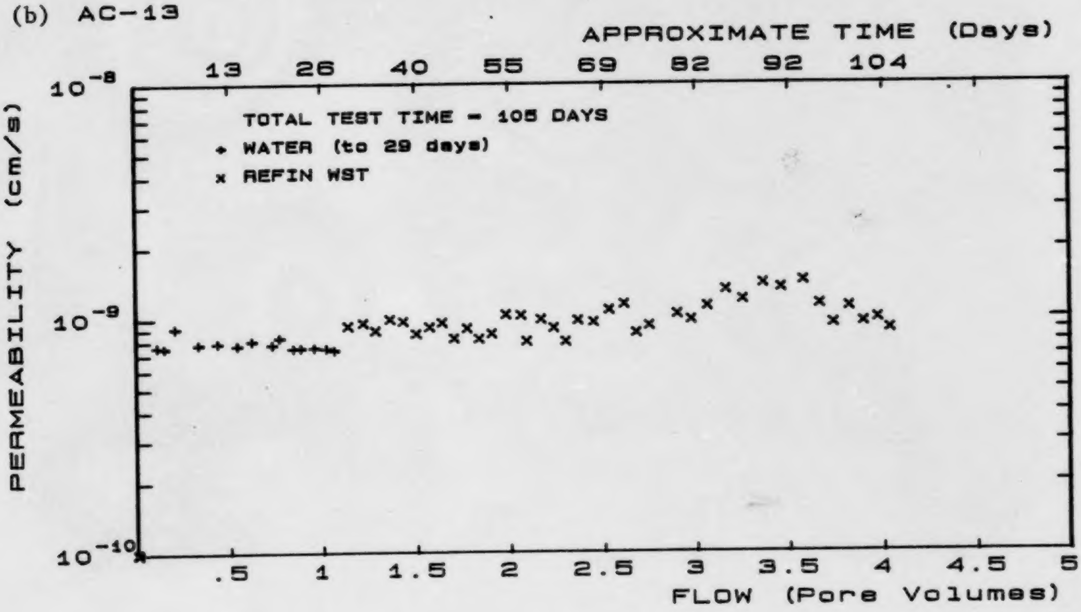


Figure 44. Permeability versus volume of flow of water and real-site refinery waste through acrylate grout. (a) Plot for sample AC-5. (b) Plot for sample AC-13.

refinery waste raised the permeability by 0.2 order of magnitude. The permeability versus pore volume flow curve stayed at that level, except for the temporary rise in the curve when the gradient was lowered to 341. However, the reintroduction of the 454 gradient brought the permeability back to a final equilibrium of 1.0 x 10^{-9} cm/sec.

As can be seen from the preceding descriptions, the permeation of real-site refinery waste had relatively little effect on the permeability of acrylate grout samples.

- Permeability Test of Acrylate Grout With 25% Sodium Hydroxide

The two acrylate samples tested with 25% sodium hydroxide were designated as AC-20 and AC-21. Their diameter was 75 mm and their thicknesses were 31 and 34 mm, respectively. Figure 45 shows the variation in their permeabilities with pore volume flow.

Both tests were started by permeating the samples with water so that a reasonable degree of saturation could be achieved. These samples were tested on water for a duration of 42 and 47 days, respectively, and for flow values of 0.31 and 0.21 pore volume, respectively. The permeability versus flow curve of sample AC-21 was quite stable, while that of AC-20, less so. However, their equilibrium permeabilities with water leveled off at about the same point, at 1.5 x 10^{-10} cm/sec for sample AC-20, and 1.8 x 10^{-10} cm/sec for sample AC-21. The tests on water were conducted at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), a net confining pressure of 121 kPa (17.5 psi), and at gradients of 340 (AC-20) and 310 (AC-21).

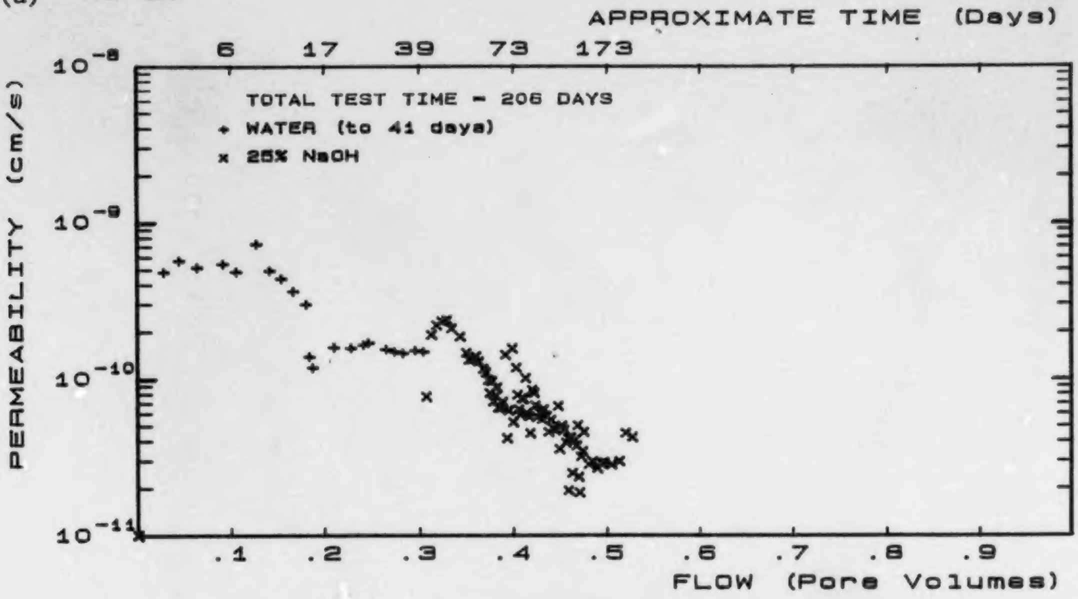
The 25% sodium hydroxide was introduced into the samples immediately following the tests with water and at pressure and gradient conditions identical to those used with water. In the case of sample AC-20, there was some scatter in the obtained data, but sample AC-21 behaved well. However, both curves actually turned down, indicating a gradual decrease in the permeability of both samples. Ultimately, the samples reached very low permeabilities of 4.3 x 10^{-11} cm/sec and 2 x 10^{-11} cm/sec, respectively. To illustrate the imperviousness of sample AC-21 with sodium hydroxide, the permeability of 2 x 10^{-11} cm/sec with a gradient of 311 resulted in 0.7 cc of flow, or 0.014 pore volume of flow over a period of one month. Thus, these samples were practically impervious toward the end of their tests. Samples AC-20 and AC-21 were on sodium hydroxide for 168 and 114 days with resulting total flows of 0.26 and 0.12 pore volume of sodium hydroxide, respectively. The plotted data show quite a scatter because in the 10^{-11} cm/sec range of permeability, the measuring apparatuses are not too accurate.

It is clear that these samples became extremely impervious to sodium hydroxide. However, it is not known what would happen to them after, say, 2 pore volumes of flow of sodium hydroxide, which could require approximately 12 years of testing.

- Permeability Test of Acrylate Grout With Xylene

Two acrylate grout samples, AC-2 and AC-9, were tested with xylene. Their diameter was 75 mm and their thicknesses were 35 and 42 mm, respective-

(a) AC-20



(b) AC-21

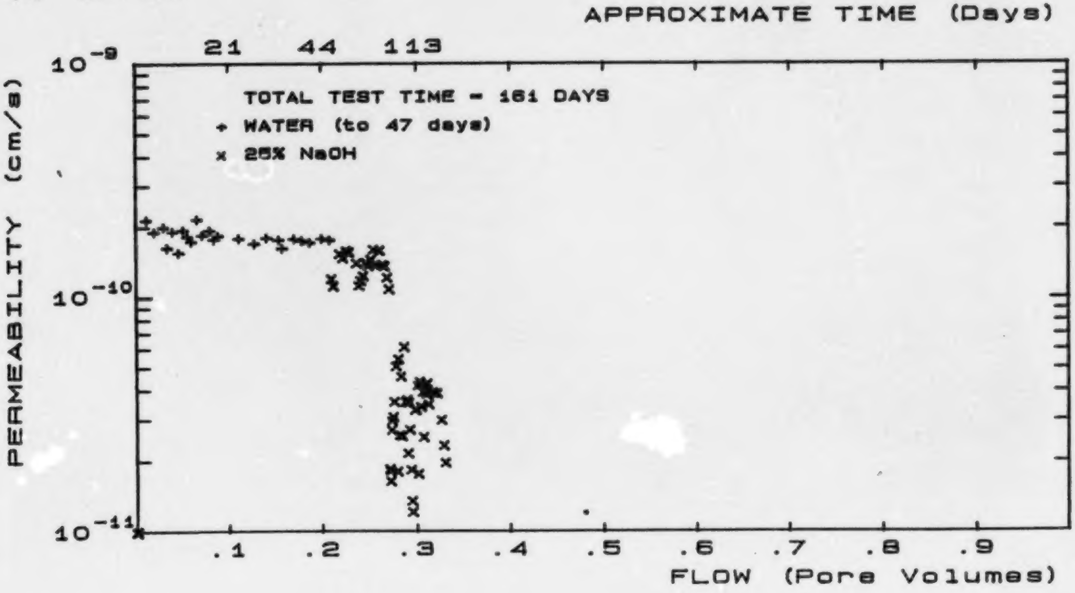


Figure 45. Permeability versus volume of flow of water and 25% sodium hydroxide through acrylate grout. (a) Plot for sample AC-20. (b) Plot for sample AC-21.

ly. Figure 46 shows the variation of permeability with pore volume flow for the samples.

In the beginning of the tests, water was percolated through the samples in order to saturate them. For the most part, sample AC-2 was permeated at a headpressure of 207 kPa (30 psi), a tailpressure of 34.5 kPa (5 psi), a net confining pressure of 155 kPa (22.5 psi), and a gradient of 503. Sample AC-9 was tested with water at a headpressure of 104 kPa (15 psi), a tailpressure of 21 kPa (3 psi), a net confining pressure of 110 kPa (16 psi), and a gradient of 201. Their permeabilities exhibited little variation with water, and the samples came to equilibrium at the permeabilities of 4.7×10^{-10} cm/sec (AC-2) and 2.2×10^{-10} cm/sec (AC-9). These permeabilities were registered at the flow values of 0.69 and 0.37 pore volume, respectively.

The xylene was introduced into sample AC-2 at a headpressure of 173 kPa (25 psi), a tailpressure of 0, a net confining pressure of 155 kPa (22.5 psi), and a gradient of 503. This caused a gradual increase in the permeability, and the sample permeability peaked at 1.4×10^{-7} cm/sec after 1.52 pore volumes of flow of xylene. After a total flow of 2.64 pore volumes and 15 days on xylene, the sample reached an equilibrium permeability of 1.3×10^{-7} cm/sec.

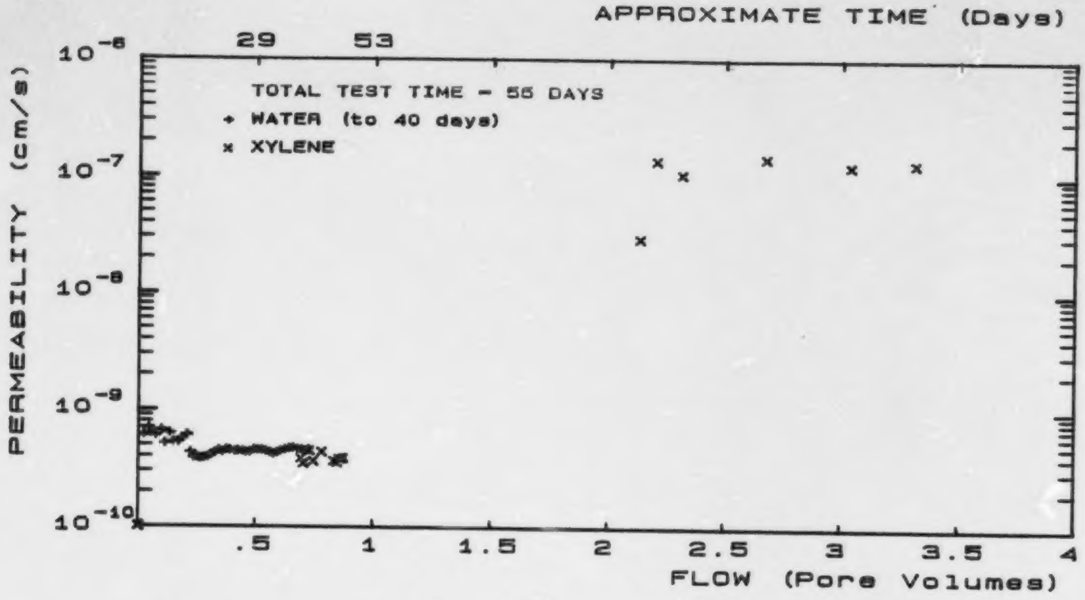
The xylene caused an abrupt increase in the permeability of sample AC-9. This sample was permeated with xylene at a headpressure of 104 kPa (15 psi), a tailpressure of 0, a net confining pressure of 121 kPa (17.5 psi), and a gradient of 251. Within 0.79 pore volume of flow of xylene, the permeability of the sample increased to 3.4×10^{-8} cm/sec, which, with continued testing, slowly climbed to a final equilibrium value of 6.26×10^{-8} cm/sec. This sample was tested for 41 days and 19.4 pore volumes of flow with xylene.

The two acrylate grout samples with xylene showed fair agreement in their final equilibrium permeabilities. Sample AC-2 ended up with a somewhat higher final permeability than sample AC-9. This may have been due to the larger hydraulic gradient used with sample AC-2, or its higher equilibrium permeability with water.

- Analysis of Permeability Test Results For Acrylate Grout

Figure 47 illustrates in a bar chart form the overall permeability changes of acrylate grout with the ten selected chemicals. On the left vertical axis of the chart permeability is plotted on a log scale. Along the horizontal axis the chart is subdivided into ten boxes, each representing one of the ten chemicals. On the right vertical axis the equilibrium permeabilities of the acrylate grout samples with water are indicated. Each shaded bar represents the average changes in the permeability of two or more acrylate grout samples with one of the chemicals. Each bar starts at the equilibrium permeability of the grout with water, and may go up or down, or remain unchanged depending on the reaction of the grout with the specific chemical. In most cases the bar first rises to a dashed line that represents the permeability of the grout at the first peak of its permeability with flow. The bar may rise further and terminate at a permeability level that corresponds to the final equilibrium permeability of the grout with specific chemical. The number on each line gives the number of pore volumes of chemical which

(a) AC-2



(b) AC-9

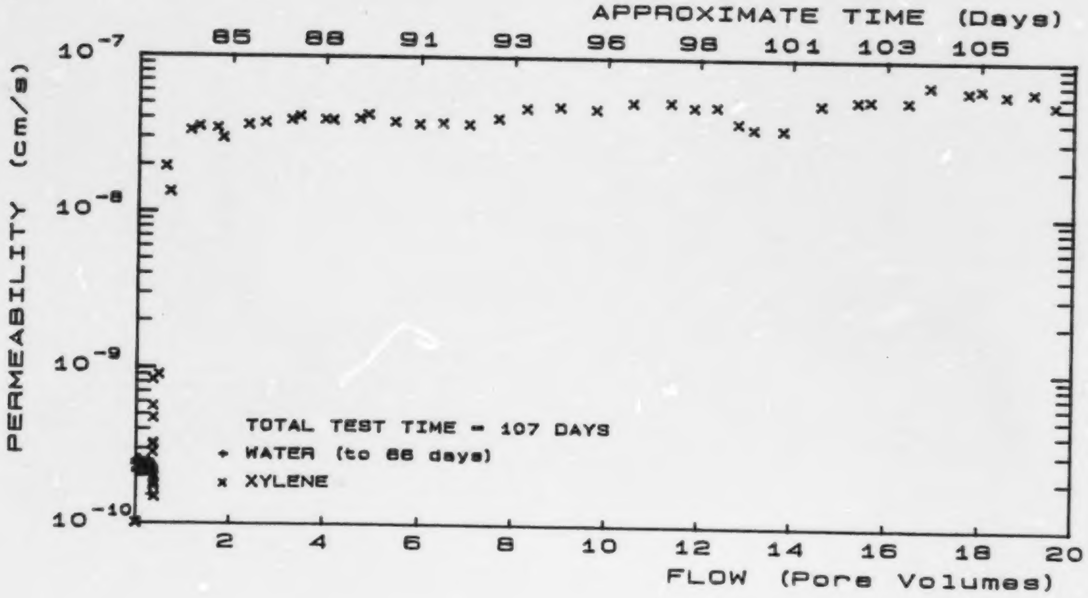


Figure 46. Permeability versus volume of flow of water and xylene through acrylate grout. (a) Plot for sample AC-2. (b) Plot for sample AC-9.

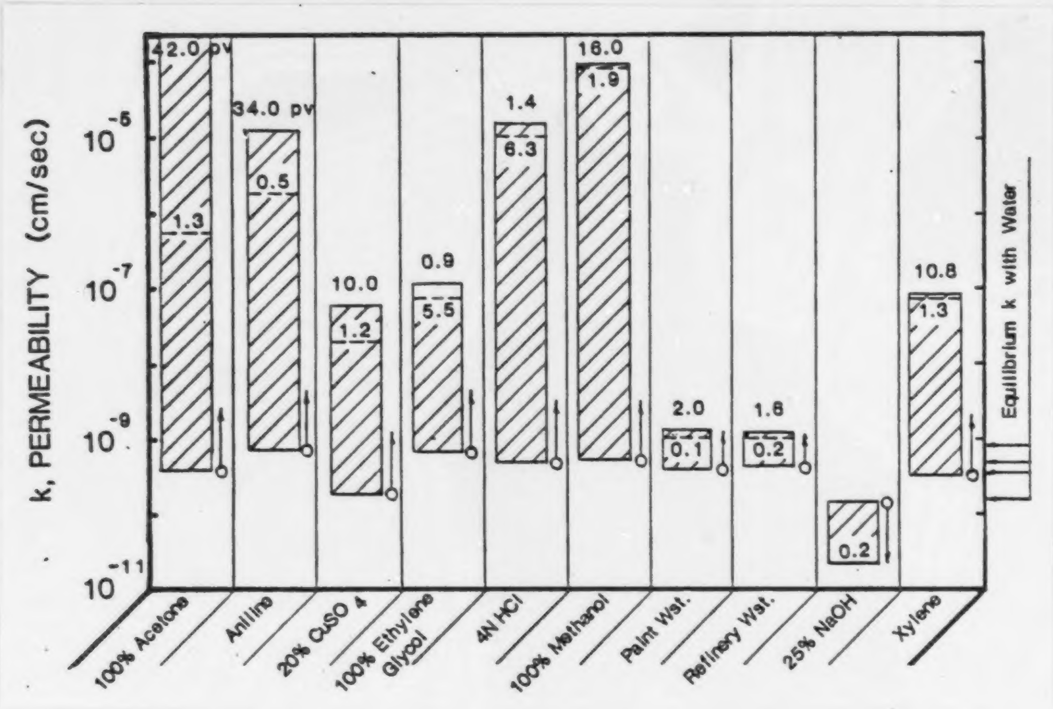


Figure 47. Permeability of acrylate grout with various chemicals.

flowed through the sample when it first reached the indicated equilibrium permeability.

As shown in the bar chart, the acrylate grout exhibited excellent resistance to real-site paint and refinery wastes, and to 25% sodium hydroxide. Its performance was satisfactory with 20% cupric sulfate, 100% ethylene glycol and 100% xylene. The 100% aniline, 100% acetone, 4N hydrochloric acid, and 100% methanol were very detrimental to the permeability of the grout. The peculiar behavior of the grout with 25% sodium hydroxide is noteworthy. With the introduction of this permeant, the permeability of the grout decreased. However, this may have been but a temporary decrease since only 0.2 pore volume of flow took place with the sodium hydroxide. It is possible that the trend may have reversed itself with more flow, but only after a very long testing time.

The effects of chemical concentration on acrylate grout can be observed in Figures 48 through 51. The figures show four pairs of permeability test plots, each figure showing two permeability versus flow curves for a selected chemical, one highly concentrated, the other more dilute.

Figure 48 illustrates the test plots for acrylate grout with 100% and 25% acetone permeants, while Figure 49 shows the test curves for acrylate with 100% and 25% methanol. In both cases the effect of the higher chemical concentration is very pronounced. In the case of methanol, its 100% solution increased the permeability of the acrylate samples by about 5.5 orders of magnitude, while the 25% methanol had practically no effect on the permeability of the grout. In the case of acetone, while the 100% acetone again caused a 5.5 orders of magnitude increase in the permeability of the acrylate grout samples, the 25% acetone solution caused only a 1.5 orders of magnitude increase.

Figure 50 shows the behavior of acrylate grout with 1N and 4N concentrations of hydrochloric acid. After having permeated the grout, both leachates caused essentially the same increase in the permeability of the samples. The hydrochloric acid in both solutions was found to be detrimental to the acrylate grout.

Finally, Figure 51 shows the permeability versus flow plots for acrylate grout with 20% and 10% solutions of cupric sulfate. The ultimate permeability of both of these samples was the same. But while the samples with the 20% solution reached their ultimate permeability within 5 pore volumes of flow, the samples with the 10% cupric sulfate reached the same permeability only after 15 pore volumes of flow. Thus the reaction of the grout was much slower with the weaker solution.

In summary, it was found from this limited data that the chemicals with reduced concentration, as compared to the ones with higher concentration, may have any of three effects on the ultimate permeability of the acrylate grout: (1) it may make the increase in grout permeability smaller, or even negligible; (2) it may cause the same increase in permeability, but delay it; or (3) it may make no difference at all. One should note that these comments only apply to the specific concentrations of chemicals. However, it is apparent that the acrylate grout reacts differently with each of the various chemicals and their various concentrations.

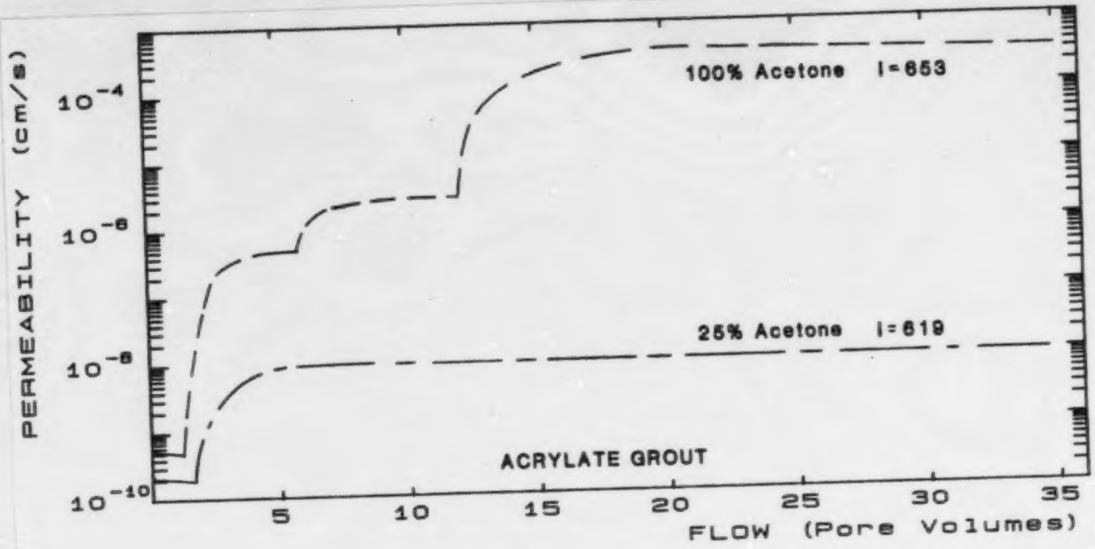


Figure 48. Permeability of acrylate grout with 100% and 25% acetone.

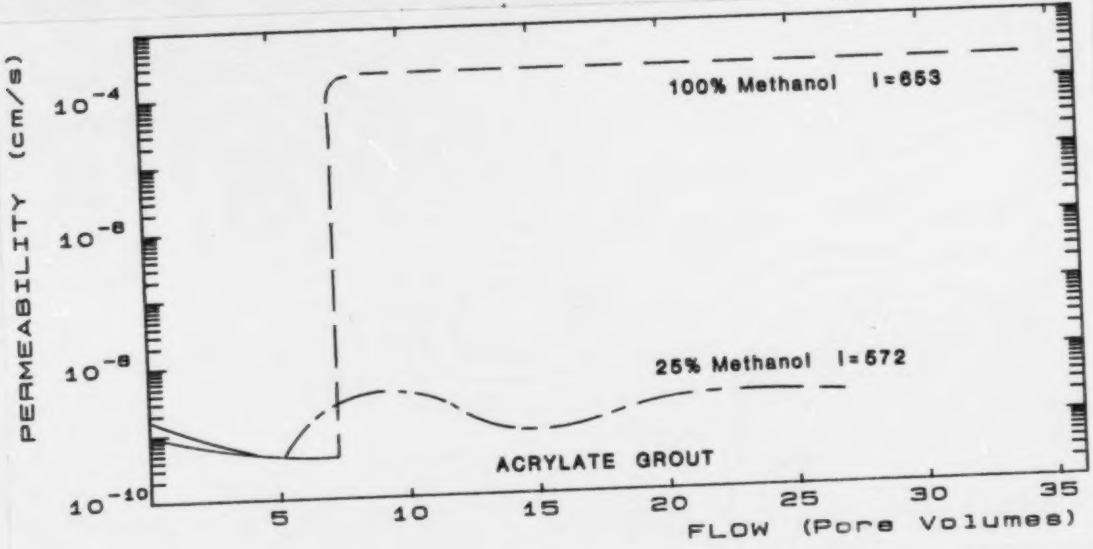


Figure 49. Permeability of acrylate grout with 100% and 25% methanol.

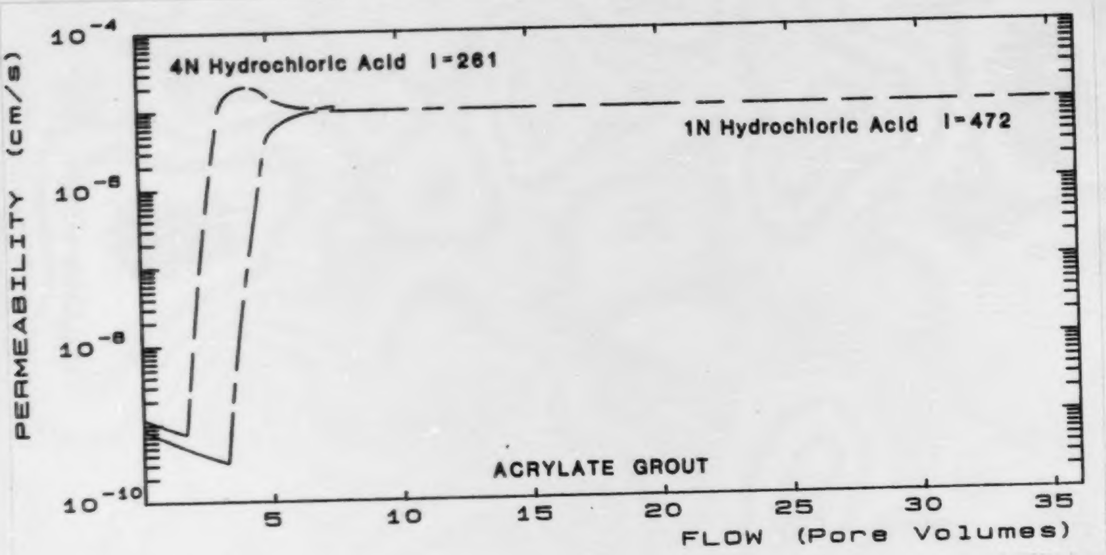


Figure 50. Permeability of acrylate grout with 1N and 4N hydrochloric acid.

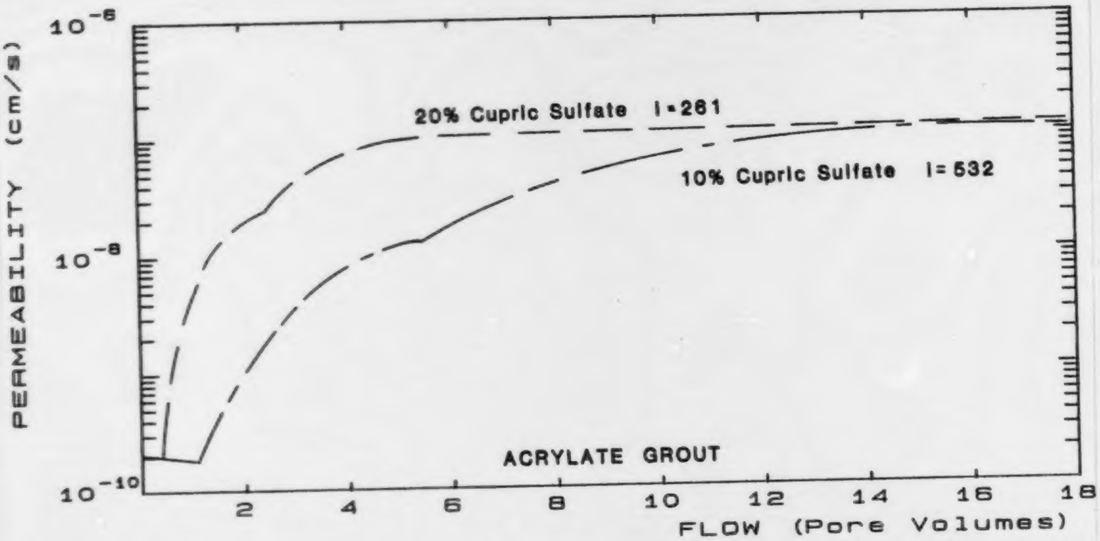


Figure 51. Permeability of acrylate grout with 20% and 10% cupric sulfate.

Permeability Tests of Cement-Bentonite (Mix 1) Grout

The cement-bentonite grout was selected as one of the grouts in this study because of its extensive use in dam cutoff construction. In this grout the cement and water provide the structure of the hardened grout, while the bentonite and water serve as the barrier in the voids of the cement structure. This grout has the advantages of being strong, potentially quite impervious, nontoxic, inexpensive, and having a long setting time. Its disadvantages are that it is made up of particulate matter that can segregate from the water and it has a high viscosity that prevents its use in finer grained soils. For the specific proportions of the components used in mixing this grout, please see Section 4.

For this test program the cement-bentonite grout samples were made by injecting the grout into pea gravel, after attempts to inject it into sand had failed. The mixing of the grout was simple, but the grouting was difficult, as the bentonite particles had a tendency to form filter cakes and block the flow. The application of higher grouting pressures could not prevent this. The grout had to be made more fluid by adding water to it, which raised its water-cement ratio. This, in turn, made the grout more pervious with water. The average baseline permeability (its permeability with water) was 3 x 10^{-6} cm/sec, a value too high for barrier construction. However, while a new and more impervious mix (cement-bentonite mix 2) was designed and tried, the permeability of mix 1 was tested to observe in general the reactions between a cement-bentonite grout and various chemicals. Specifically, the permeability of this grout was tested with deionized water, 100% acetone, 100% ethylene glycol, 100% methanol, real-site paint waste, real-site refinery waste, and 100% xylene. In most cases just one sample was tested since the baseline permeability was high and only general trends were sought.

The cement-bentonite (mix 1) samples made were consistent with respect to appearance and permeability. They had a gray color and were hard. Because of their relatively high permeability, the samples were made thick, averaging 82 mm in thickness.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With Deionized Water

There were no cement-bentonite (mix 1) samples that were tested with water alone. However, a number of the samples were tested with water over a large number of pore volumes before they were tested with chemicals. All 8 samples that were tested with chemicals were first saturated with water, and all except one had a pore volume flow of more than 2.0. In fact, the average flow of the samples with water was 8.4 pore volumes. As shown on Figures 52 through 58, the portion of the permeability versus flow curves with water were for the most part well behaved, some completely level, others gently sloping at a small and constant rate. A typical example was sample CB-8, which was tested with water over 17.5 pore volumes of flow, and during this flow its permeability increased from 2 x 10^{-6} to 3.4 x 10^{-6} cm/sec. Using the equilibrium or final permeability values with water, the average permeability of the cement-bentonite (mix 1) grout samples was 3.0 x 10^{-6} cm/sec. Their median permeability was 3.5 x 10^{-6} cm/sec. The permeabilities of these grout samples were quite consistent with water.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With 100% Acetone

One cement-bentonite (mix 1) grout sample, CB-10, was tested with 100% acetone. Its thickness was 48 mm and its diameter was 75 mm. Figure 52 shows the permeability versus flow plot for the sample.

The cement-bentonite sample was first permeated with water to saturate it. This was accomplished in a falling-head type permeability apparatus with a headpressure of approximately 6.9 kPa (1 psi), and with zero backpressure. The approximate applied net confining pressure was 38 kPa (5.5 psi) and the gradient was approximately 15. The average permeability of the sample with water was 1.6 x 10^{-6} cm/sec. The sample had a total testing time of three days and 2.2 pore volumes of flow of water.

The 100% acetone was introduced into the sample at pressure and gradient conditions that were identical to those used with water. The acetone caused the permeability of the sample to rise at a moderate rate with flow to a first plateau where a permeability of 8.2 x 10^{-6} cm/sec was reached after a pore volume flow of 4.1 of acetone. With continued flow, the permeability continued to rise at a slow but steady rate and after a pore volume flow of 14.5 of acetone, the permeability reached 2.1 x 10^{-5} cm/sec and the test was terminated. Although this cement-bentonite sample did not reach a final equilibrium, the decision to terminate the test was based on the relatively small rise in the curve with the large volume of flow that had taken place with acetone.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With 100% Ethylene Glycol

One cement-bentonite (mix 1) grout sample, CB-3, was tested with 100% ethylene glycol. Its thickness was 44 mm, and its diameter 75 mm. Figure 53 shows the permeability versus flow plot for the sample. Preceding the introduction of ethylene glycol, the sample was saturated with water. The water permeation through the sample was accomplished at a net confining pressure of 242 kPa (35 psi), a backpressure of 0, and a headpressure of approximately 6.9 kPa (1 psi) in a falling-head type permeability apparatus. The sample was tested with a gradient of approximately 16. The permeability of the sample with water started out at 2.5 x 10^{-6} cm/sec and gradually rose to 3.2 x 10^{-6} cm/sec, by which time 19.8 pore volumes of water had flowed through the sample.

The 100% ethylene glycol was permeated through the sample at a headpressure of 21 kPa (3 psi), a tailpressure of 0, a net confining pressure of 166 kPa (24 psi), and at a gradient of 48. With the introduction of ethylene glycol, the permeability of the sample dropped off sharply to a low value of 1.3 x 10^{-7} cm/sec, which occurred after 3.0 pore volumes of flow of ethylene glycol. With an additional flow of 5.0 pore volumes of ethylene glycol, the permeability rose to 4 x 10^{-7} cm/sec and, with minor fluctuations, stayed around this value until the end of the test. The average of the last four readings was 4.2 x 10^{-7} cm/sec after a total accumulated flow of 55 pore volumes of ethylene glycol.

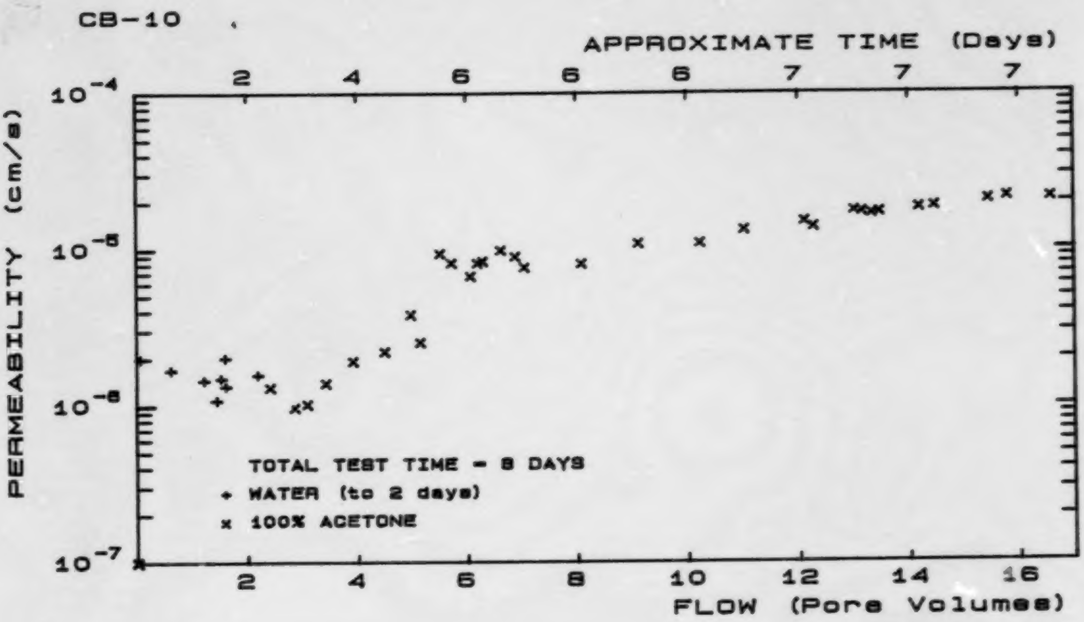


Figure 52. Permeability versus volume of flow of water and 100% acetone through cement-bentonite (mix 1) grout. Plot for sample CB-10.

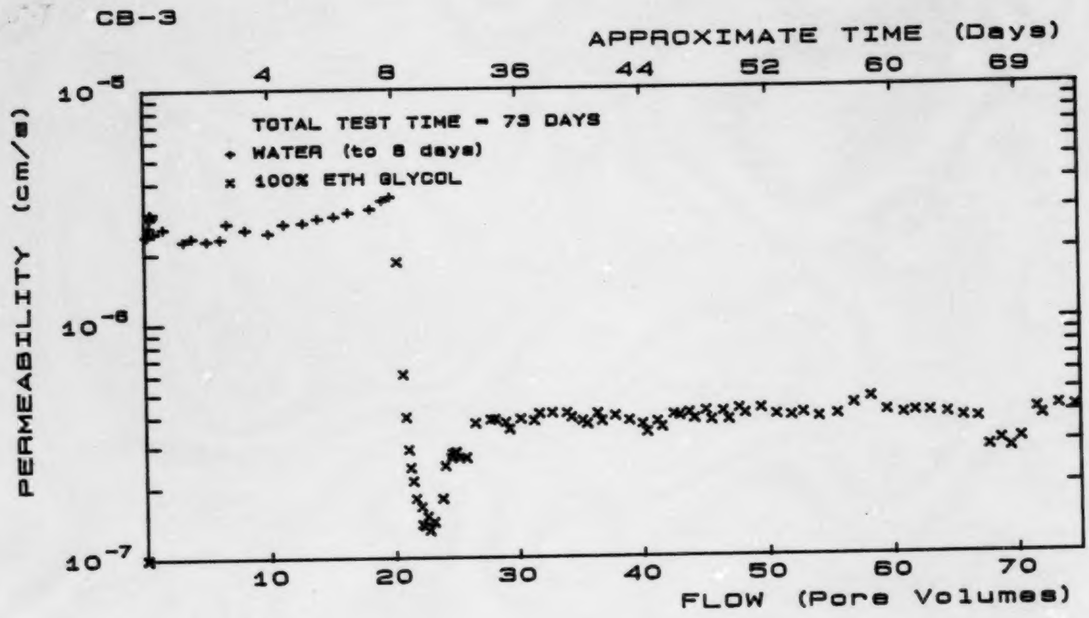


Figure 53. Permeability versus volume of flow of water and 100% ethylene glycol through cement-bentonite (mix 1) grout. Plot for sample CB-3.

As can be seen in Figure 53, the permeability versus flow curve with ethylene glycol showed rather sharp initial fluctuations, but after approximately 8 pore volumes of flow of ethylene glycol the curve leveled off and the sample exhibited a stable permeability to the end of the test, by which time 55 pore volumes of flow had taken place.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With 100% Methanol

One cement-bentonite (mix 1) grout sample, designated CB-14, was tested with 100% methanol. Its thickness was 101 mm, and its diameter 75 mm. Figure 54 illustrates the permeability versus flow plot for the sample.

The cement-bentonite sample was first permeated with water in a falling-head type permeability apparatus with a headpressure of approximately 6.9 kPa (1 psi), a backpressure of 0, a net confining pressure of 100 kPa (14.5 psi) and a gradient of 7. The permeability versus flow curve with water was found to be fairly uniform and level. The sample had a total flow of 3.9 pore volumes of water and had an average permeability of 1.3 x 10^{-6} cm/sec.

The methanol was introduced into sample CB-14 at a headpressure of 104 kPa (15 psi), a backpressure of 0, and a net confining pressure of 121 kPa (17.5 psi). The driving gradient was 104. The introduction of methanol into sample CB-14 caused an immediate drop in the permeability of the sample. The permeability decreased to 5.1 x 10^{-7} cm/sec with 2.6 pore volumes of flow of methanol. It stayed around this value until an accumulated flow of 5 pore volumes on methanol, then it started to rise and came to a plateau with a permeability of 1 x 10^{-6} cm/sec after 7.2 pore volumes of flow of methanol. From there on, with some minor fluctuation, the sample permeability stayed at the same level. The test was terminated after 21.6 pore volumes of flow with methanol and with a final average permeability of 1 x 10^{-6} cm/sec.

These writers believe that the permeability test results obtained on sample CB-14 are representative reactions of the cement-bentonite (mix 1) grout to methanol. As mentioned above, the sample was tested extensively over more than 21 pore volumes of flow with methanol and came to a fairly stable equilibrium permeability.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With Real-Site Paint Waste

The cement-bentonite (mix 1) grout sample tested with real-site paint waste was sample CB-8. Its thickness was 68 mm, and its diameter 75 mm. Figure 55 shows the permeability versus flow plot for the sample.

In order to saturate the cement-bentonite sample before its test with paint waste, water was permeated through it in a falling-head type permeability test apparatus. The headpressure used was approximately 6.9 kPa (1 psi), the backpressure was 0, and the net confining pressure was 238 kPa (34.5 psi). A gradient of approximately 10 was applied. The sample exhibited a uniform and slowly increasing permeability on water that rose from 2 x 10^{-6} cm/sec to approximately 3.5 x 10^{-6} cm/sec just prior to the introduction of paint waste. The sample was tested for a total pore volume flow of 18.1 with

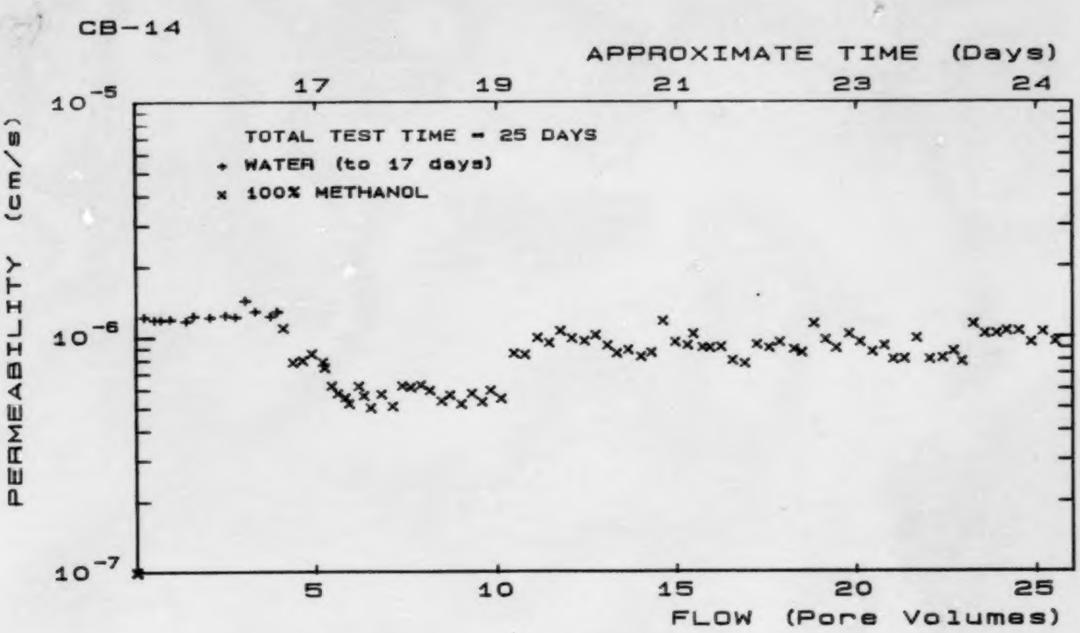


Figure 54. Permeability versus volume of flow of water and 100% methanol through cement-bentonite (mix 1) grout. Plot for sample CB-14.

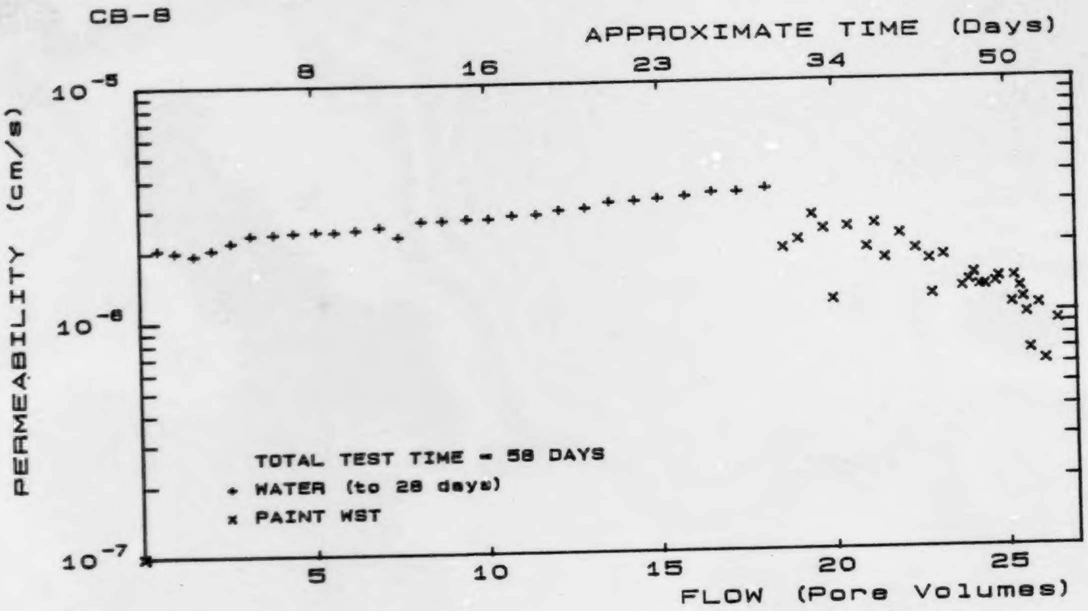


Figure 55. Permeability versus volume of flow of water and real-site paint waste through cement-bentonite (mix 1) grout. Plot for sample CB-8.

water.

The permeability testing of the sample with real-site paint waste was accomplished at essentially the same pressure conditions as used with water, except the net confining pressure was changed from 238 to 204 kPa (34.5 to 29.5 psi). When the paint waste was introduced into the sample, its permeability started to drop immediately and the permeability decreased more or less continuously to a low of 6.3 x 10^{-7} cm/sec after 8.3 pore volumes of flow on paint waste. At this point, the test was terminated. It is speculated that this decrease in permeability would have continued had the test not been terminated, since the gradual decrease in permeability may have been due to the blocking effect of microorganisms that were growing in the waste. It is reasonable to assume that these microorganisms became lodged in the voids of the grouted sample and, having accumulated there, caused a decrease in its permeability.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With Real-Site Refinery Waste

One cement-bentonite (mix 1) grout sample, CB-13, was tested with real-site refinery waste. Its thickness was 118 mm, and its diameter 75 mm. Figure 56 shows the permeability versus flow plot for the sample.

This cement-bentonite sample was first permeated with water. This was accomplished in a falling-head permeability apparatus with a headpressure of approximately 6.9 kPa (1 psi), a backpressure of 0, an effective confining pressure of approximately 100 kPa (14.5 psi), and a gradient of approximately 6. As shown in Figure 56, this sample exhibited an exceptionally level permeability versus flow curve with water. After only 0.76 pore volume of flow the sample reached an equilibrium permeability of 1.7 x 10^{-6} cm/sec which it maintained to the end of its test with water, after a total of 2.7 pore volumes of flow of water.

The real-site refinery waste was permeated through the sample at a headpressure of 21 kPa (3 psi), a backpressure of 0, and a net confining pressure of 162 kPa (23.5 psi). A gradient of 18 was used. With the introduction of refinery waste, the permeability of the sample decreased quite rapidly with flow. It reached a level low portion of 1.7 x 10^{-7}cm/sec after approximately 1.0 pore volume of flow on refinery waste. This was followed by minor fluctuations in the permeability versus flow curve until an accumulated pore volume flow of 5.6 with the refinery waste was reached. At that point the permeability started to decrease again and at the termination of the test reached a low value of 9.6 x 10^{-8} cm/sec. The test was terminated at an accumulated flow of 6.4 pore volumes of refinery waste. During testing, microorganisms were observed growing in the head line and, therefore, it is speculated that the downturn in permeability with increasing flow was probably due to the blockage of flow through the sample by microorganisms that most likely were deposited in the voids of the grouted soil sample.

- Permeability Test of Cement-Bentonite (Mix 1) Grout With Xylene

Three cement-bentonite (mix 1) grout samples, CB-9, CB-11, and CB-12,

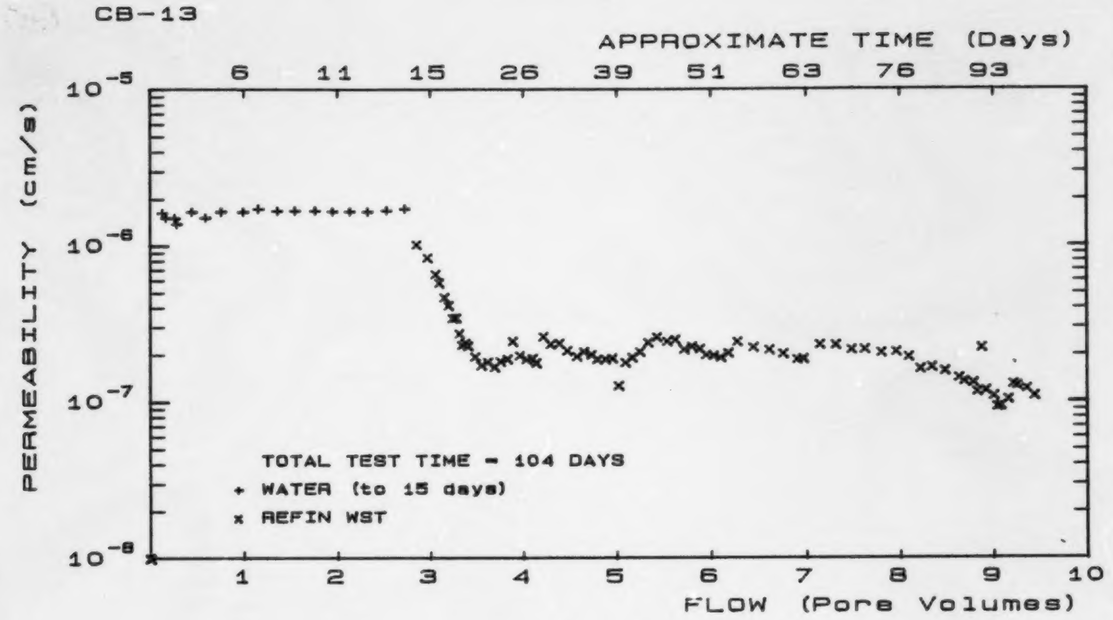


Figure 56. Permeability versus volume of flow of water and real-site refinery waste through cement-bentonite (mix 1) grout. Plot for sample CB-13.

were tested with xylene. Their thicknesses were 59, 105, and 110 mm, respectively, and all three were 75 mm in diameter. Figures 57 and 58 show the permeability versus flow plots for the three samples.

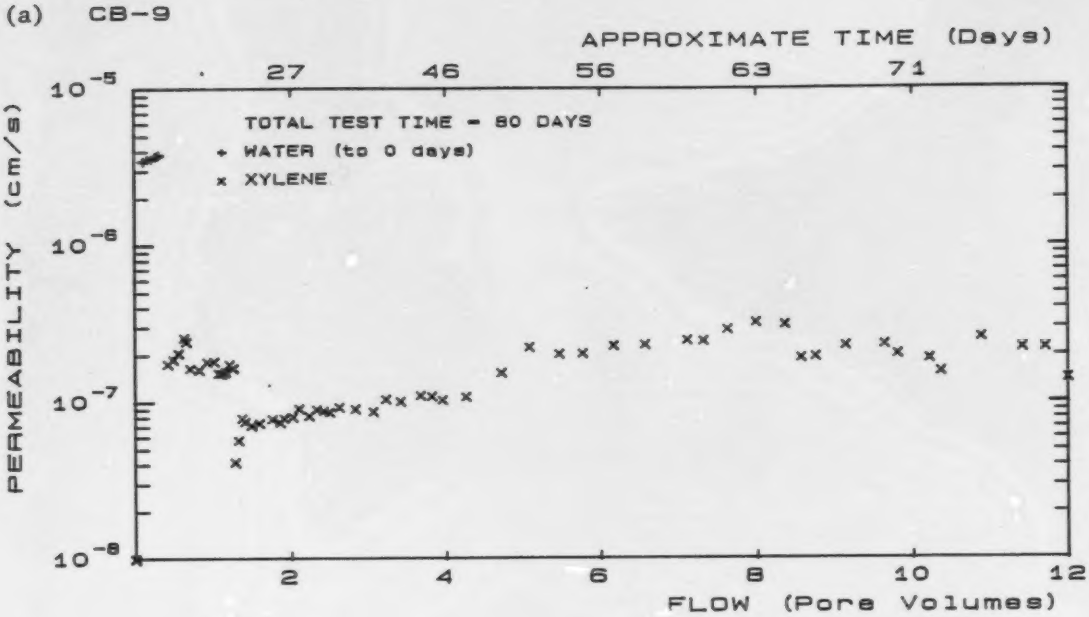
Preceding the introduction of xylene, all three samples were saturated with water. The water was introduced into sample CB-9 in a falling-head type permeability apparatus with a headpressure of approximately 6.9 kPa (1 psi), a tailpressure of 0, a net confining pressure of 135 kPa (19.5 psi), and at a gradient of approximately 12. The plot of permeability versus flow on water for this sample was fairly level with a permeability value of 3.7×10^{-6} cm/sec over 0.31 pore volume of flow.

The xylene was initially introduced into sample CB-9 at essentially the same head conditions as were used with water, except the net confining pressure was increased to 204 kPa (29.5 psi). It can be observed in Figure 57(a) that when the xylene was introduced, the permeability of the sample dropped from 3.7×10^{-6} cm/sec with water to a low of 1.5×10^{-7} cm/sec after 0.8 pore volume of flow of xylene. At that point in the test, the headpressure was changed to approximately 14 kPa (2 psi), the net confining pressure to 235 kPa (34 psi), and the gradient to 24. With that, the permeability of the sample temporarily dropped even further, reaching a low of 4.2×10^{-8} cm/sec, then rising to 7.6×10^{-8} cm/sec after 1.1 pore volumes of flow of xylene. From there on, the permeability of sample CB-9 started a very slow rise with flow that peaked at a value of 3.3×10^{-7} cm/sec after a total of 7.7 pore volumes of flow of xylene. With further flow, the permeability decreased slightly and came to a fairly stable equilibrium at 2.1×10^{-7} cm/sec. The test was terminated after a total flow of 11.7 pore volumes with xylene.

Samples CB-11 and CB-12 were first permeated with water. For each sample, this was accomplished in a falling-head permeability apparatus at an approximate headpressure of 6.9 kPa (1 psi), a backpressure of 0, a net confining pressure of 100 kPa (14.5 psi), and with a gradient of approximately 6.5. As can be observed in Figures 57(b) and 58, both samples had very stable permeability versus flow curves with water. Sample CB-11 had a final equilibrium permeability of 5.5×10^{-6} cm/sec after an accumulated flow of 17 pore volumes of water. Sample CB-12 had a final equilibrium permeability of 3.5×10^{-6} cm/sec after an accumulated flow of 3.4 pore volumes of water.

The xylene was introduced into sample CB-11 basically with the same pressure and gradient conditions as were used with water, except the confining pressure was increased to 238 kPa (34.5 psi). With the introduction of xylene, the permeability immediately dropped to 2.1×10^{-8} cm/sec. At that point, the headpressure was increased to 14 kPa (2 psi), while the gradient was increased to 13. This resulted in a slight rise in the permeability of the sample. The headpressure was subsequently increased to 21 kPa (3 psi), and the gradient to 20. This resulted in a further increase in the permeability to 3×10^{-7} cm/sec. With continued flow, the permeability began to descend gradually and at the termination of the test, after a total pore volume flow of 0.34 with xylene, it reached a low value of 1.1×10^{-7} cm/sec.

(a) CB-9



(b) CB-11

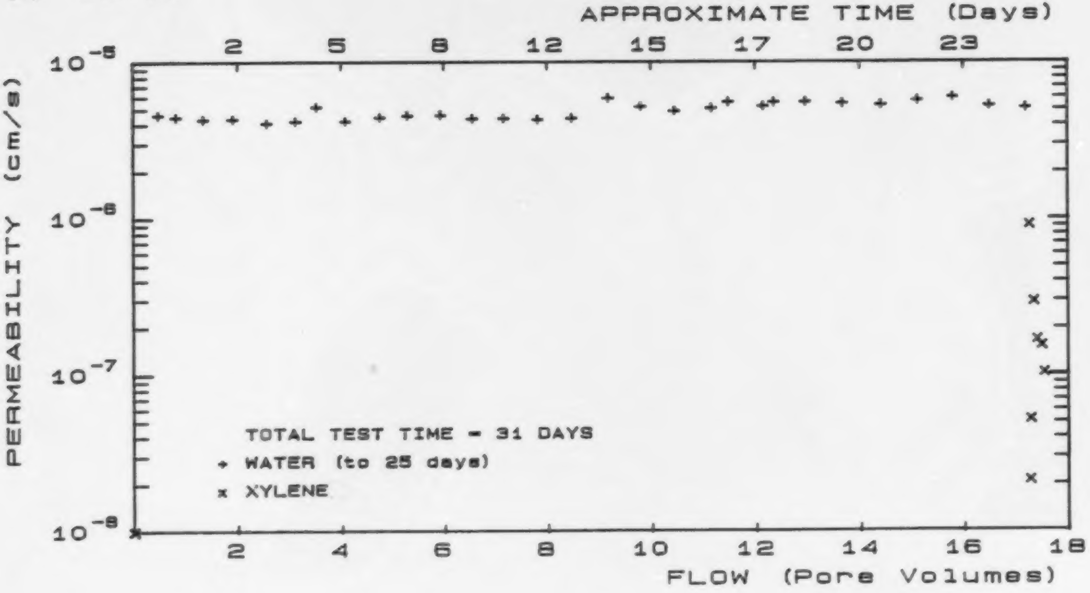


Figure 57. Permeability versus volume of flow of water and xylene through cement-bentonite (mix 1) grout. (a) Plot for sample CB-9. (b) Plot for sample CB-11.

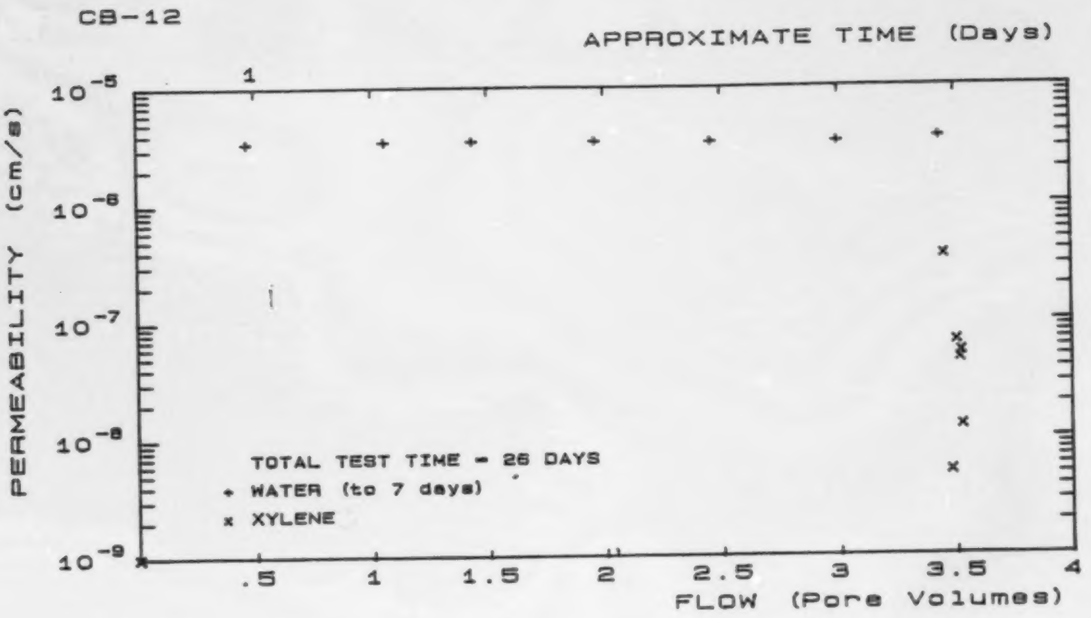


Figure 58. Permeability versus volume of flow of water and xylene through cement-bentonite (mix 1) grout sample CB-12.

The xylene was introduced into sample CB-12 at a headpressure of 14 kPa (2 psi), a backpressure of 0, a net confining pressure of 235 kPa (34 psi), and a gradient of 13. The xylene caused the permeability of the sample to drop from 3.5 x 10^{-6} cm/sec with water to 5.4 x 10^{-9} cm/sec with only 0.04 pore volume of flow. Following this period, the permeability of the sample rose to an average of 4.6 x 10^{-8} cm/sec for the last four readings. The test was terminated at an accumulated flow of 0.09 pore volume of xylene.

Unfortunately, neither sample CB-11 nor CB-12 was tested long enough with xylene. Therefore, the results from their tests cannot be used to fully substantiate the equilibrium permeability obtained on sample CB-9. However, the similarity of their initial reactions to xylene fully support those found for sample CB-9; hence, they serve a limited but useful purpose.

- Analysis of Permeability Test Results For Cement-Bentonite (Mix 1) Grout

The cement-bentonite (mix 1) grout was tested with six chemical permeants to determine if any changes would take place in its permeability. The chemicals included 100% acetone, 100% ethylene glycol, 100% methanol, real-site paint waste, real-site refinery waste, and reagent grade xylene. Figure 59 shows the permeability test results in a bar chart form. For an explanation of the nature of the chart, refer to the section entitled Analysis of Permeability Test Results for Acrylate Grout which was presented previously.

As illustrated in the chart, the cement-bentonite grout was moderately pervious with water, and not very consistent. Its permeability varied between 1.3 x 10^{-6} cm/sec and 5 x 10^{-6} cm/sec. These being relatively high values, the grout is probably not suitable for use in hazardous waste cutoff construction. However, in order to obtain general information on the reactivity of the cement-bentonite grout with the various chemicals, it was subjected to a series of six permeability tests.

The introduction of 100% acetone caused the permeability of the cement-bentonite (mix 1) grout to increase by a little over one order of magnitude. With 100% ethylene glycol, paint waste, refinery waste, and xylene the permeability of the grout actually decreased from the values obtained with water. With xylene this amounted to a decrease of almost two orders of magnitude. The permeation of 100% methanol had practically no effect on the permeability of the grout.

When the samples were tested with paint waste and refinery waste, it was observed that microorganisms were growing in the leachate lines leading to the samples. It is believed that once the organisms reached the fine pores of the samples they blocked them, and reduced the size of the passageways available for the leachates. Thus the permeability of the grout samples was found to decrease gradually.

Overall, the cement-bentonite (mix 1) grout samples had disappointingly high permeabilities with water. On the other hand, the six chemicals had relatively modest detrimental effects on this grout, in fact, in four cases the permeability of the grout decreased with chemical flow.

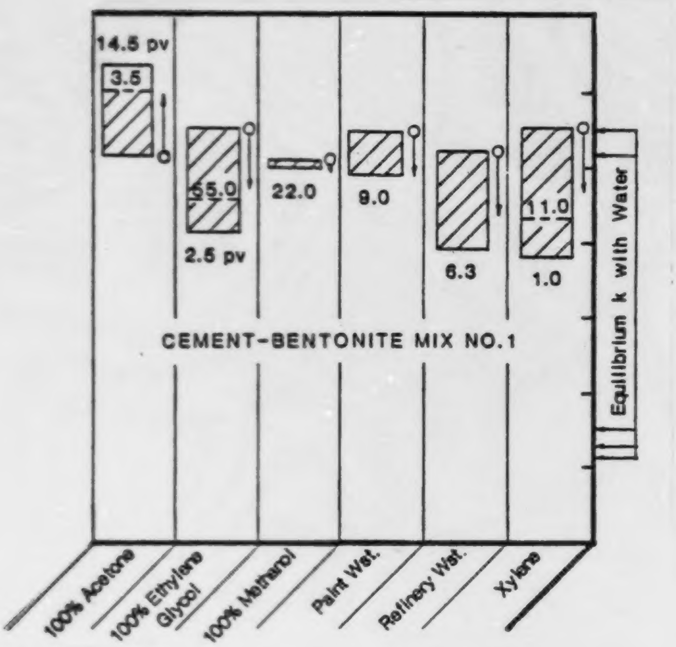


Figure 59. Permeability of cement-bentonite (mix 1) grout with various chemicals.

Permeability Tests of Cement-Bentonite (Mix 2) Grout

The cement-bentonite (mix 2) grout was designed to have a much lower permeability with water than the cement-bentonite (mix 1) grout. This was achieved by using a low water to cement ratio for mix 2. This resulted in an increased viscosity of the mix, which was alleviated by the addition of a super-plasticizer. As with mix 1, the grout was nontoxic, easy to mix, had an adequately long setting time, and cured to a hard consistency. The viscosity of the grout still required that it be injected into pea gravel in making the samples. The resulting samples were very uniform with respect to color, hardness and permeability with water. The samples were made to measure 75 mm in diameter and approximately 42 mm in thickness. Their average permeability with water was 2.3 x 10^{-10} cm/sec, a very low value. These samples were tested at a relatively high gradient in order to reduce the testing time to a reasonable time span.

The cement-bentonite (mix 2) grout samples were tested with deionized water, 100% acetone, reagent grade aniline, 20% solution of cupric sulfate, 4N solution of hydrochloric acid, 100% methanol, and 25% solution of sodium hydroxide. In four of these cases no duplicates were tested, because the testing times were exceptionally long and no additional test stations could be made available.

◦ Permeability Test of Cement-Bentonite (Mix 2) Grout With Deionized Water

No cement-bentonite (mix 2) grout samples were tested with water alone. However, all samples were saturated and tested with water before the introduction of chemicals, with an average water flow of 0.66 pore volume.

The initial portions of the test plots in Figures 60 through 66 show that most of the test curves with water had an initially downward sloping shape that leveled off after a small amount of flow. A typical example was sample CB-22 (Figure 64), which started out with water at a permeability of 9 x 10^{-10} cm/sec. With continued testing the permeability of the sample decreased, first moderately fast, then more slowly, and finally came to an equilibrium at 2 x 10^{-10} cm/sec after 0.65 pore volume of flow with water. Using the equilibrium or final permeability values of nine grout samples with water, the mean value of their permeability was found to be 2.3 x 10^{-10} cm/sec, a very low value. The median value of permeability was 2 x 10^{-10} cm/sec. The permeabilities of the nine cement-bentonite (mix 2) grout samples with water were deemed consistent.

◦ Permeability Test of Cement-Bentonite (Mix 2) Grout With 100% Acetone

One cement-bentonite (mix 2) grout sample, designated as CB-28, was tested with 100% acetone. The thickness of the sample was 44 mm, and its diameter was 75 mm. Figure 60 shows the permeability test plot for the sample.

The sample was first saturated with water. At the beginning of the test, the water was permeated through the sample at a headpressure of 173 kPa (25 psi), a backpressure of 69 kPa (10 psi), and a net confining

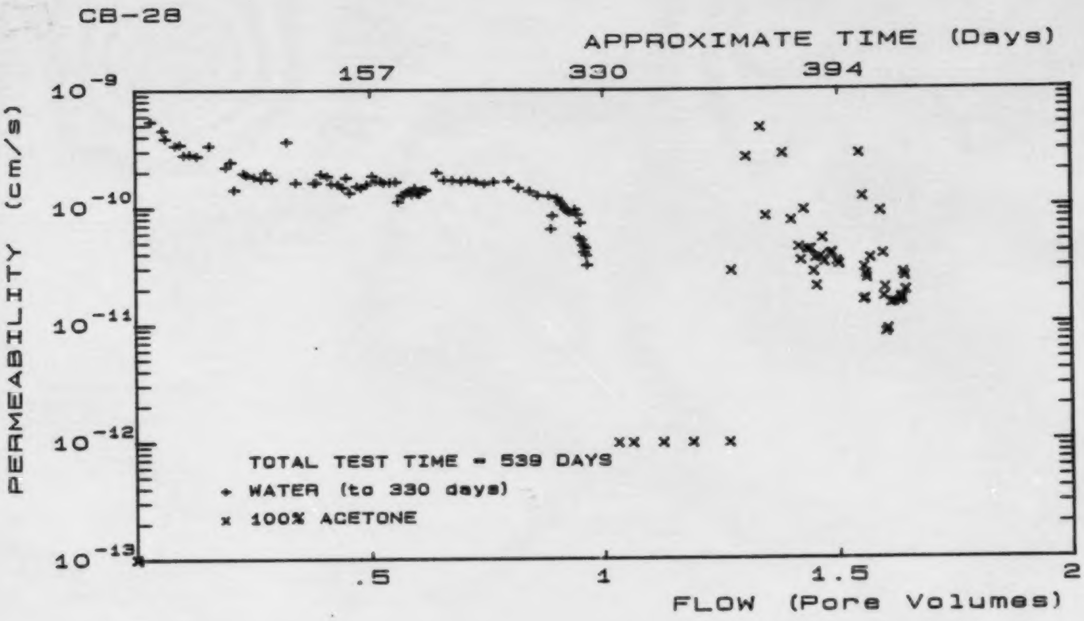


Figure 60. Permeability versus volume of flow of water and 100% acetone through cement-bentonite (mix 2) grout. Plot for sample CB-28.

pressure of 121 kPa (17.5 psi). The gradient of flow was 240. In the later stages of the test, the net driving pressure was increased to 173 kPa (25 psi) by reducing the backpressure to 0, which resulted in an increase in the gradient to 399. One may observe in Figure 60 that during the initial stages of water permeation the permeability was gradually decreasing with flow. Following that, the permeability came to an equilibrium at 1.7 x 10^{-10} cm/sec between pore volume flows of 0.5 and 0.8. Afterwards, still with water, the permeability started to decrease again, first gradually, then more rapidly. During the last 0.07 pore volume of flow, the permeability dropped very rapidly from 1.2 x 10^{-10} to 3.3 x 10^{-10} cm/sec. From the appearance of the curve, it seems that the sample was becoming plugged and was approaching an impervious state with water.

The 100% acetone was introduced into the sample at pressure and gradient conditions which were essentially identical to those used in the later stages with water, that is, the headpressure was 242 kPa (35 psi), the backpressure 69 kPa (10 psi), and the net confining pressure 121 kPa (17.5 psi). The driving gradient was 399. In the later stages of the test on acetone, both the headpressure and tailpressure were dropped by 69 kPa (10 psi), still maintaining a driving pressure of 73 kPa (25 psi) and a gradient of 399. When the acetone was introduced into the sample, many erratic readings resulted. Some of these were exhibited as negative flow readings in the tail line of the testing apparatus which were attributed to small leaks in the line. The sample was later removed from this faulty station and placed into a new one. With an accumulated flow of 0.09 pore volume with acetone in the new station, the sample still exhibited slightly decreasing permeabilities with flow. At the termination of the test the permeability dropped to 2.1 x 10^{-11} cm/sec after a total accumulated flow of 0.68 pore volume with 100% acetone.

As can be seen, this cement-bentonite (mix 2) grout sample was quite impervious to both water and acetone. During the 209 days of testing on acetone, the sample showed a trend of decreasing permeability. There was no indication that this trend might reverse itself and that the sample might suffer a loss in its imperviousness at a later time. Since the testing of this sample took 539 days, there was not time left to continue its testing, nor to test a replicate of this sample.

- Permeability Test of Cement-Bentonite (Mix 2) Grout With Aniline

One grout sample, CB-30, was tested with reagent grade aniline. Its thickness was 45 mm, and its diameter 75 mm. Figure 61 illustrates the permeability versus pore volume flow curve for this sample.

Before the introduction of aniline into the sample, it was permeated with water. The testing started with a headpressure of 173 kPa (25 psi), a backpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). The gradient of the flow was 234. For the last quarter of the flow on water, the headpressure was increased to 242 kPa (35 psi), which resulted in an increase in the gradient to 391. It may be observed on the water segment of the permeability versus flow curve that the permeability was initially decreasing at a fairly fast rate, then it slowed down and arrived at an equilibrium permeability of 1.4 x 10^{-10} cm/sec after 0.67 pore volume of

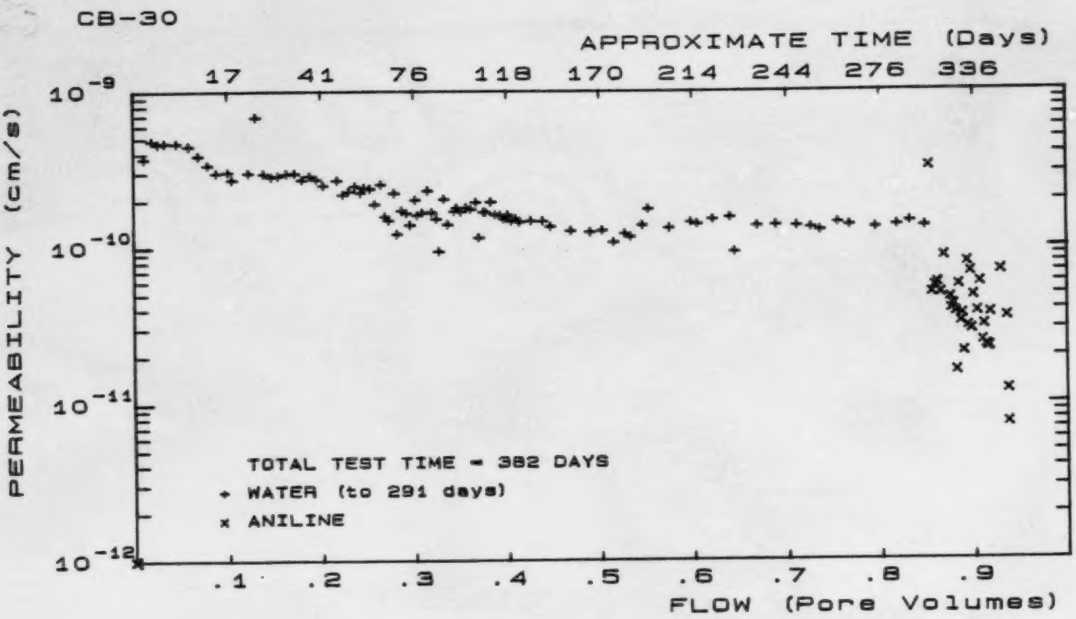


Figure 61. Permeability versus volume of flow of water and aniline through cement-bentonite (mix 2) grout. Plot for sample CB-30.

flow. This permeability was maintained to the end of the test with water, that is, until 291 days and 0.4 pore volume had passed.

The aniline was introduced into sample CB-30 at essentially the same pressure and gradient conditions as were used in the later stages of testing with water. As seen in Figure 61, with the introduction of aniline, the permeability of the sample started to decrease immediately and, with a flow of only 0.01 pore volume of aniline, it dropped to a value of 5.2×10^{-11} cm/sec. With continued flow, the permeability continued to decrease and after 91 days and 0.1 pore volume of flow of aniline, the last reading on this sample gave a permeability of 7.6×10^{-12} cm/sec, indicating a practically impervious sample. The sample at that time was not at equilibrium with respect to permeability, but there was not time left to continue the testing of this sample.

As can be observed, at the termination of its test the cement-bentonite (mix 2) grout exhibited impervious behavior with aniline. The permeability versus flow curve for sample CB-30 showed a continuous trend of decreasing permeability over a test period of 382 days. Again, no replicates were tested because of the long testing time and the lack of available test stations.

- Permeability Tests of Cement-Bentonite (Mix 2) Grout With 20% Cupric Sulfate

Three cement-bentonite (mix 2) grout samples, CB-18, CB-19, and CB-29, were tested with 20% cupric sulfate. Their thicknesses were 35, 35, and 37 mm, respectively. All three samples were 75 mm in diameter. Figures 62 and 63 show the permeability versus flow plots for the three samples.

Preceding the introduction of cupric sulfate, the three samples were permeated with water in order to saturate them. The samples were tested at a net confining pressure of 121 kPa (17.5 psi), a headpressure of 173 kPa (25 psi), and a backpressure of 69 kPa (10 psi). Samples CB-18 and CB-19 were both tested with water at a gradient of 301 for 55 days and to accumulated flows of 0.18 and 0.12 pore volumes of water, respectively. Sample CB-29 was tested with water for 68 days with an accumulated flow of 0.69 pore volume, and at a gradient of 285. For samples CB-18 and CB-19, with some fluctuations, the permeability with water decreased throughout the test. At the end, their permeabilities reached the low values of 7×10^{-11} cm/sec and 6.2×10^{-11} cm/sec, respectively. Sample CB-29 exhibited an initially decreasing permeability with flow, however, its permeability leveled off and came to an equilibrium at 3.9×10^{-10} cm/sec toward the end of its permeation with water.

The 20% cupric sulfate was introduced into samples CB-18 and CB-19 at pressure and gradient conditions that were identical to those used in their tests with water. With cupric sulfate, the flow in both samples came to a complete halt, that is, these samples became totally impervious to cupric sulfate. For plotting purposes, the dummy permeability value of 1×10^{-12} cm/sec was assigned to the no-flow test readings.

Sample CB-29 was initially permeated with 20% cupric sulfate at the same pressure and gradient conditions as were used in its test with water. After

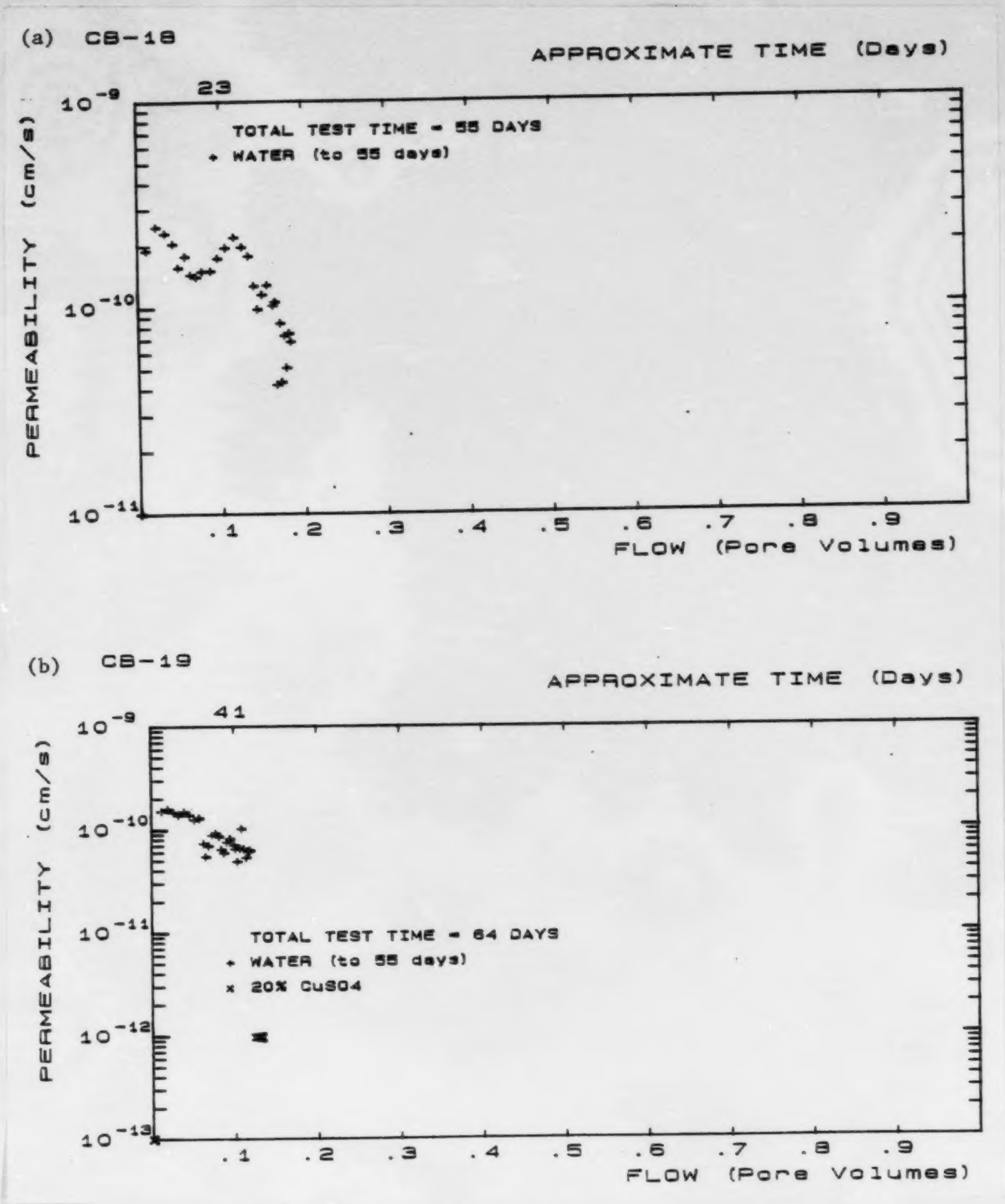


Figure 62. Permeability versus volume of flow of water and 20% cupric sulfate through cement-bentonite (mix 2) grout. (a) Plot for sample CB-18. (b) Plot for sample CB-19.

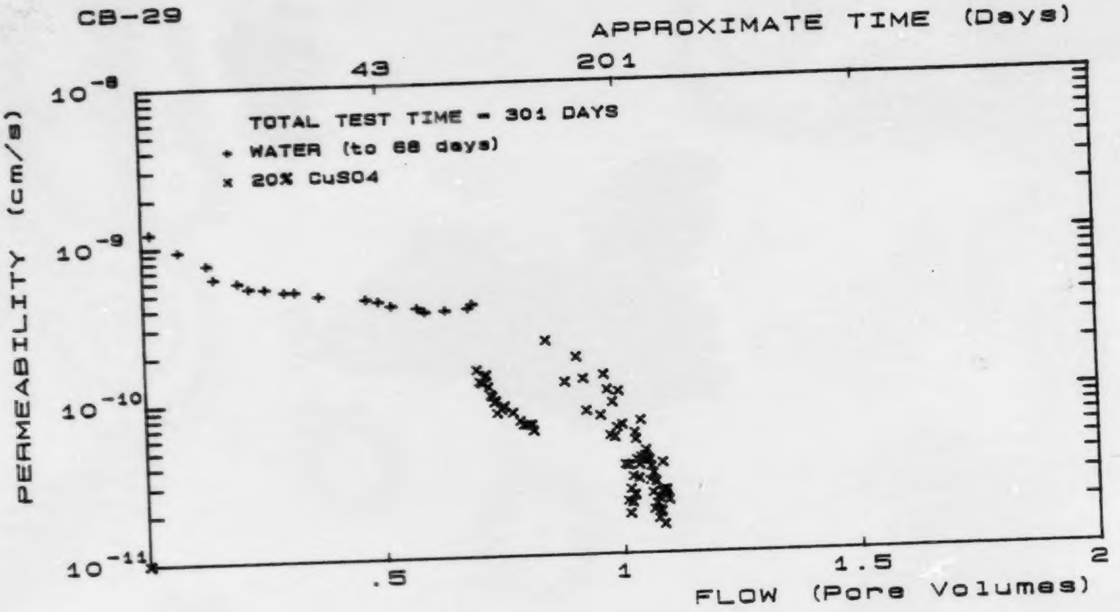


Figure 63. Permeability versus volume of flow of water and 20% cupric sulfate through cement-bentonite (mix 2) grout sample CB-29.

only 0.12 pore volume of flow of cupric sulfate, the permeability of the sample dropped to 6.3×10^{-11} cm/sec. At that time, the headpressure on the chemical was increased from 173 to 242 kPa (25 to 35 psi) and the gradient from 285 to 475. This caused an immediate increase in the permeability of the sample; however, with further flow, the permeability again started to decrease and the downward trend continued to the end of the test. After 233 days of testing and a pore volume flow of 0.4 of cupric sulfate the test was terminated. At that point, the permeability of the sample reached a low value of between 1.5 and 2.5×10^{-11} cm/sec, meaning the sample became practically impervious.

In general, all three cement-bentonite (mix 2) samples exhibited very low, nearly impervious permeability values with 20% cupric sulfate. Even if this grout would begin to disintegrate and become more pervious with continued flow of cupric sulfate, it is estimated that this would occur only after a very long time of exposure.

- Permeability Test of Cement-Bentonite (Mix 2) Grout With 4N Hydrochloric Acid

One cement-bentonite (mix 2) grout sample, designated as CB-22, was tested with 4N hydrochloric acid. Its thickness was 45 mm, and its diameter 75 mm. Figure 64 shows the permeability versus pore volume flow test plot for the sample.

Preceding the introduction of 4N hydrochloric acid, the sample was permeated with water. This was accomplished for the most part using a headpressure of 173 kPa (25 psi), a backpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). These conditions resulted in a flow gradient of 234. At the very end of testing with water, the backpressure was dropped to 0, which increased the driving pressure to 173 kPa (25 psi), and the gradient to 391. The permeability test on this sample with water resulted in a permeability versus flow curve that was smooth and exhibited a gradually decreasing permeability that finally equilibrated at a value of 2.1×10^{-10} cm/sec after 0.6 pore volume of flow of water. The complete test with water lasted 313 days and resulted in the permeation of a total of 1.17 pore volumes of water.

The 4N hydrochloric acid was introduced into sample CB-22 at the same pressure and gradient conditions as were used in the latter portion of the test with water. The introduction of hydrochloric acid caused the permeability of the sample to drop quite rapidly to a low value of 2.3×10^{-11} cm/sec after only 0.04 pore volume of flow of hydrochloric acid. After that, the flow of hydrochloric acid practically ceased. This no-flow condition was represented by the dummy permeability value of 1×10^{-12} cm/sec on the test plot. The test was terminated after 30 days at that level of permeability. The total flow of hydrochloric acid was measured to be 0.07 pore volume during 89 days of testing.

As can be seen from the data, the cement-bentonite (mix 2) grout was practically impervious with 4N hydrochloric acid. The sample showed continuously lower and lower permeabilities with hydrochloric acid, with no indication for a reversal in permeability. There were no replicates of this test,

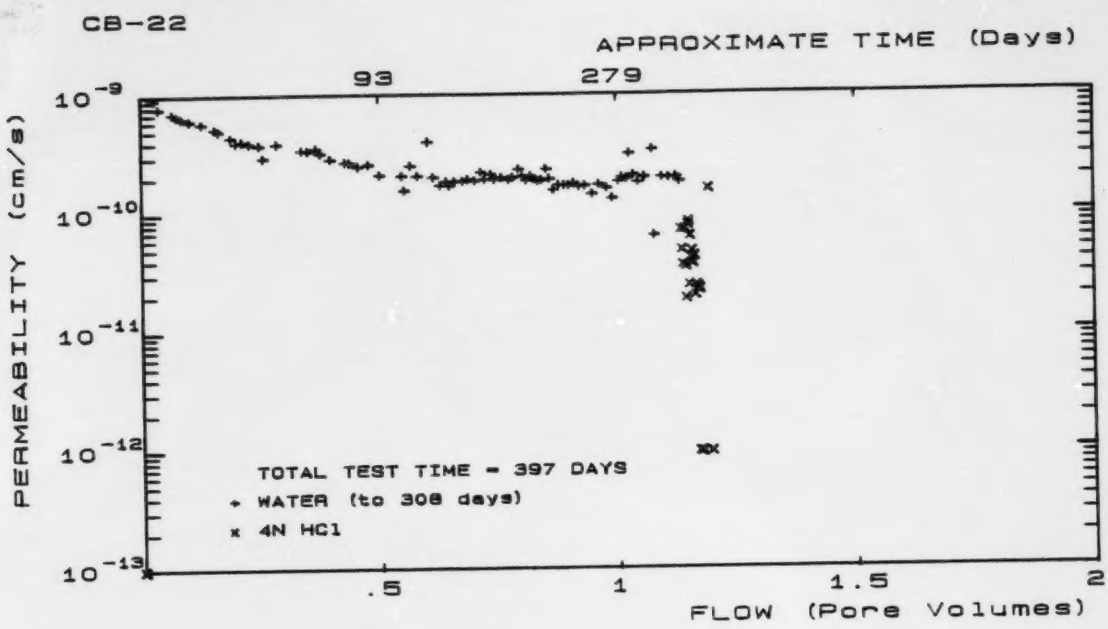


Figure 64. Permeability versus volume of flow of water and 4N hydrochloric acid through cement-bentonite (mix 2) grout. Plot for sample CB-22.

the reason being that the test tied up the permeability equipment for a total testing time of 402 days.

- Permeability Test of Cement-Bentonite (Mix 2) Grout With 100% Methanol

One cement-bentonite (mix 2) grout sample, designated as CB-31, was tested with 100% methanol. This sample had a thickness of 44 mm, and a diameter of 75 mm. Its permeability versus flow curve is shown in Figure 65.

Before the introduction of methanol, sample CB-31 was permeated with water in order to saturate it. This was accomplished first at a headpressure of 173 kPa (25 psi), a backpressure of 69 kPa (10 psi), a net confining pressure of 121 kPa (17.5 psi), and a gradient of 240. Later in the test with water, the backpressure was decreased to 0, thus increasing the driving pressure to 173 kPa (25 psi) and the gradient to 399. The permeability versus flow curve exhibited a moderate and gradual decrease at the beginning of the test on water, then seemed to have come to an equilibrium permeability at 1.8 x 10^{-10} cm/sec, which lasted from 0.5 to 0.8 pore volume of flow of water. At that point, the permeability of the sample again started to drift lower. At the end of the test with water, the permeability decreased to a low of 1.1 x 10^{-10} cm/sec after an accumulated flow of 0.96 pore volume and 305 days of testing with water.

The 100% methanol was introduced into sample CB-31 at the same pressure and gradient conditions that were used with water. With the introduction of methanol, the permeability of the sample dropped off to a low value of 4.4 x 10^{-11} cm/sec after an accumulated flow of 0.04 pore volume of methanol. Following that, the permeability of the sample increased slightly and reached a permeability of 6.1 x 10^{-11} cm/sec after an accumulated flow of 0.23 pore volume of methanol. At that point the test was terminated. In looking at the test plot in Figure 65, in the very last segment of the plot, one may detect a slight trend of increasing permeability with flow. In retrospect, it would have been desirable to continue the testing of this sample with methanol; however, because of its very low permeability, the duration of testing was excessive (442 days) and there was no time or testing space left to continue.

- Permeability Test of Cement-Bentonite (Mix 2) Grout With 25% Sodium Hydroxide

Two cement-bentonite (mix 2) grout samples, CB-23 and CB-26, were tested with 25% sodium hydroxide. Both samples were 75 mm in diameter and their thicknesses were 53 and 41 mm, respectively. Figure 66 shows the permeability versus flow plots for the two samples.

Preceding the introduction of sodium hydroxide, the two samples were saturated with water. The water permeation through both samples was accomplished at a net confining pressure of 121 kPa (17.5), a headpressure of 173 kPa (25 psi), and a backpressure of 69 kPa (10 psi). Sample CB-23 was tested at a gradient of 199 for 64 days and with 0.53 pore volume of water flow, while sample CB-26 was permeated for 67 days with an accumulated flow of 0.39 pore volume of water, and at a gradient of 257. Both samples exhibited decreases in their permeabilities with water. The rate of decrease was high at first, but became more gradual with increasing flow.

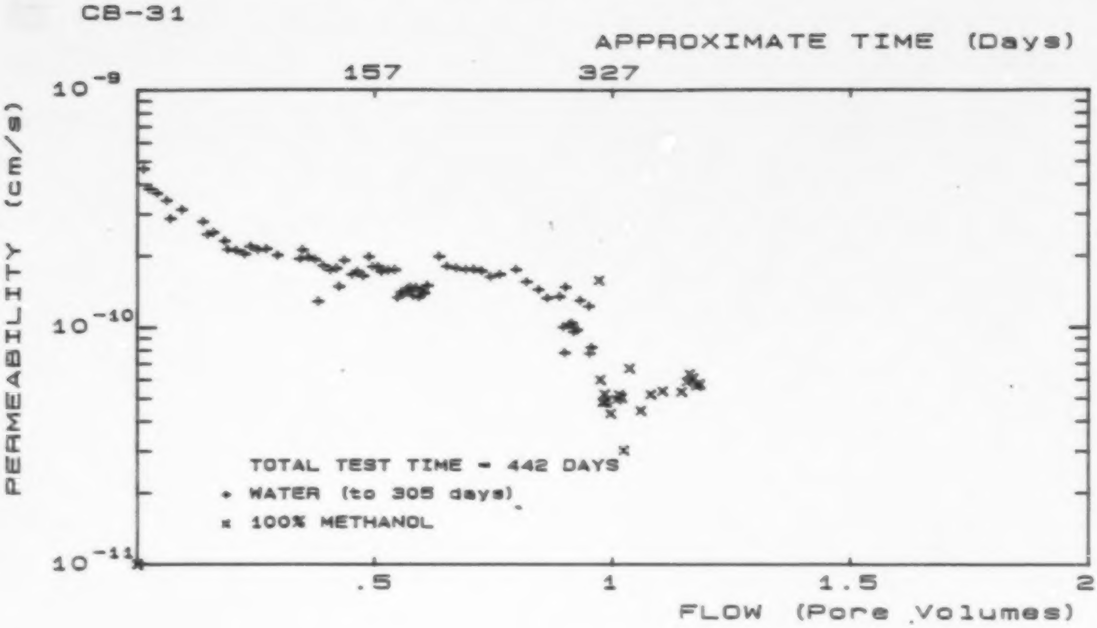
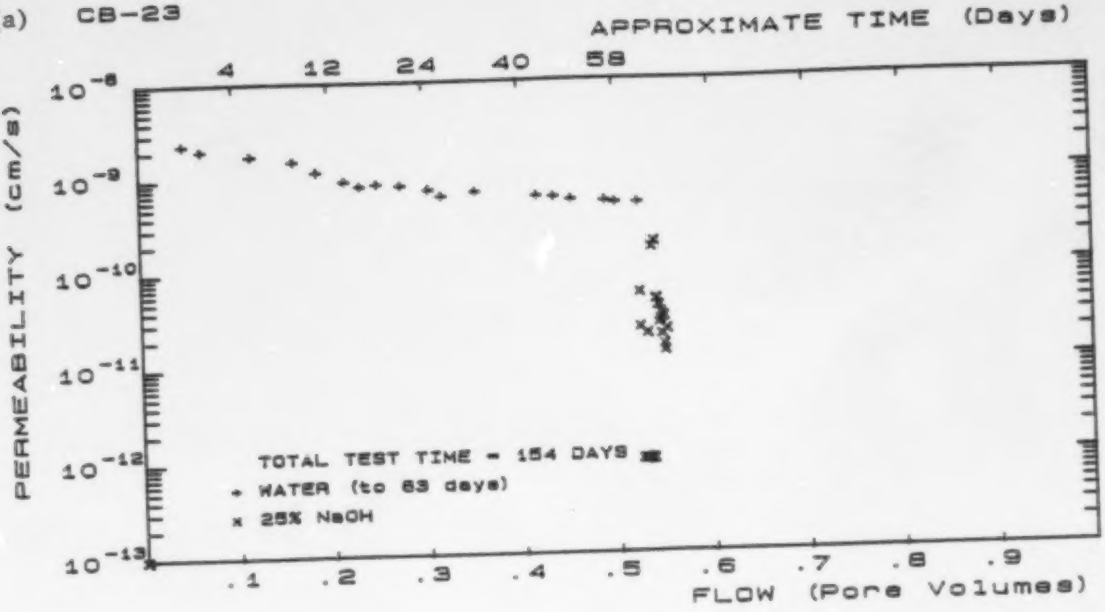


Figure 65. Permeability versus volume of flow of water and 100% mehtanol through cement-bentonite (mix 2) grout. Plot for sample CB-31.

(a)



(b)

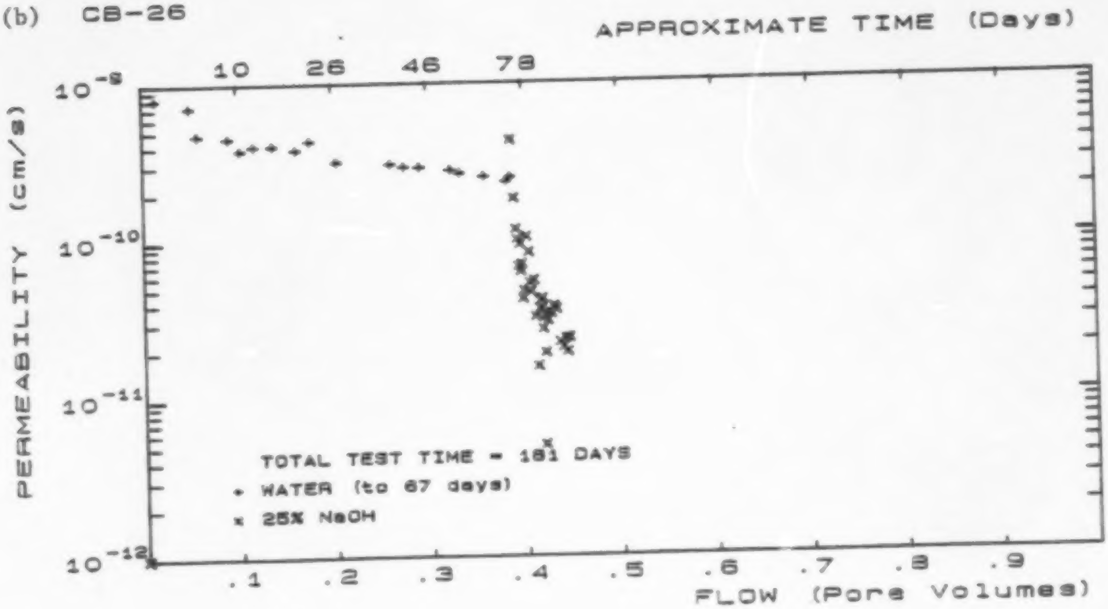


Figure 66. Permeability versus volume of flow of water and 25% sodium hydroxide through cement-bentonite (mix 2) grout. (a) Plot for sample CB-23. (b) Plot for sample CB-26.

The final permeabilities with water, 5 x 10^{-10} cm/sec and 2.5 x 10^{-10} cm/sec, respectively, are not equilibrium values, but are estimated to be close to equilibrium.

The 25% sodium hydroxide was introduced into the samples at pressure conditions and gradients identical to those used with water. With the introduction of sodium hydroxide, the permeabilities of both samples started to drop immediately and, with some fluctuations, continued to decrease to their terminal values of approximately 2 x 10^{-11} cm/sec and 2.4 x 10^{-11} cm/sec, respectively. Both these samples became practically impervious. Sample CB-23 allowed only 0.02 pore volume of flow of sodium hydroxide in 50 days of testing at a gradient of 199. Similarly, sample CB-26 had only 0.06 pore volume of flow of sodium hydroxide during a long period of 114 days of continuous testing with a hydraulic gradient of 257.

As can be seen from the previous discussion, these cement-bentonite grout samples became practically impervious during their tests with 25% sodium hydroxide. They were tested for a period of four and six months, respectively, that resulted in very little flow in spite of high driving gradients. It is not actually known whether the permeability would have turned around and increased with continued flow. However, to be sure of that, the samples would have to be tested for a very long time.

- Analysis of Permeability Test Results For Cement-Bentonite (Mix 2) Grout

The permeability of cement-bentonite (mix 2) grout was tested with deionized water and six chemicals. The results from the test with water were compared to those with chemicals to determine the effects of the chemicals on the permeability of the grout. The results of the tests are summarized in the bar chart shown in Figure 67 (for the notations used, see the section titled Analysis of Permeability Test Results for Acrylate Grout). As can be seen, with both water and chemicals, this grout was the most impervious of all the grouts tested.

Specifically, the cement-bentonite (mix 2) grout exhibited excellent permeabilities with deionized water, as its equilibrium permeability was between 2 x 10^{-10} cm/sec and 4 x 10^{-10} cm/sec.

The cement-bentonite (mix 2) grout samples were tested with the following chemicals: 100% acetone, reagent grade aniline, 20% solution of cupric sulfate, 4N solution of hydrochloric acid, 100% methanol, and 25% solution of sodium hydroxide. The introduction of every chemical caused the permeability of the grout samples to decrease from their baseline permeability with water. With very small flows of between 0.1 and 0.6 pore volume, the permeabilities dropped to approximately 3 x 10^{-11} cm/sec, or to a practically impervious state. These samples were tested on the average for 122 days with chemicals. It is of course possible that given enough time, some of the chemicals would destroy this grout, however the indications are that it would take very long testing times to answer this question, even with the use of high gradients.

In summary, the cement-bentonite (mix 2) grout had a very low permeabil-

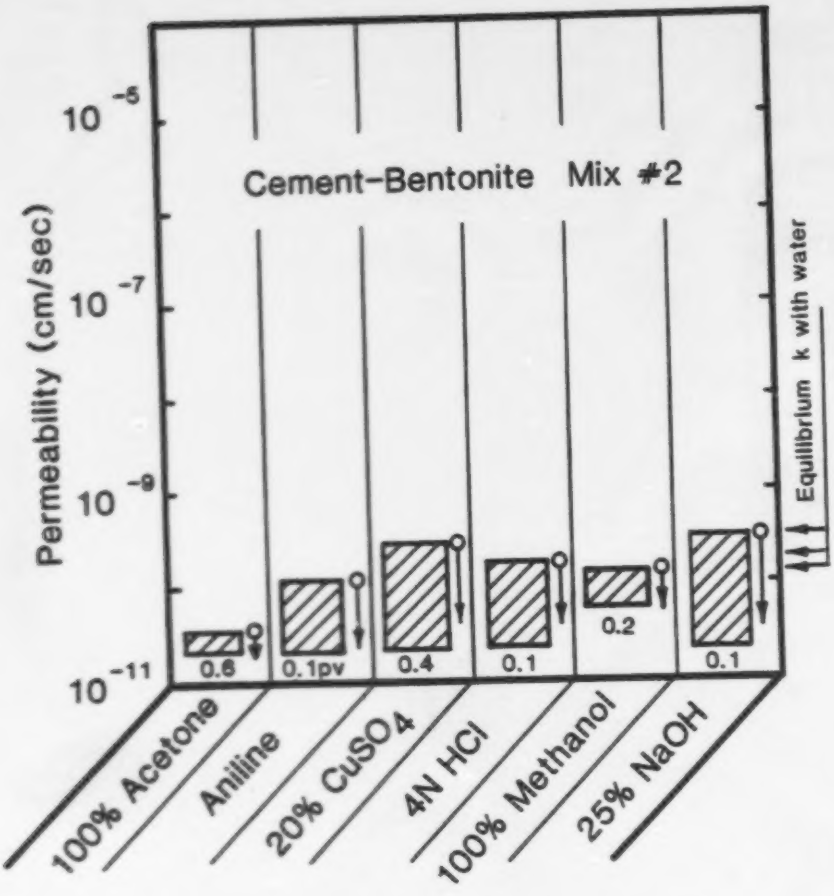


Figure 67. Permeability of cement-bentonite (mix 2) grout with various chemicals.

ity with water, and exhibited very low and decreasing permeabilities with the six chemical permeants.

Permeability Tests of Sodium Silicate Grout

Sodium silicate grout was chosen for testing in this program because it is one of the most common grouts in engineering use. This grout is an excellent choice for reinforcing weak soils and for underpinning structures. This grout is easy to mix, it is nontoxic, has low viscosity and therefore it is easy to inject even into fine sands. Its setting time can be conveniently controlled, and after having set, it quickly hardens to a strong mass. However, as far as its permeability is concerned, the sodium silicate grout was a disappointment. Its average equilibrium permeability with water was 5 x 10^{-5} cm/sec, too high a value for cutoff applications.

The sodium silicate grout samples were made by injecting the grout into a fine sand. Initially the grout was injected into a medium silica sand, but those samples quickly deteriorated with water flow due to syneresis, thus the newer samples were made with fine brown sand. The resulting samples were brown in color and were very hard. They were 75 mm in diameter and had an average thickness of approximately 65 mm.

In this study the sodium silicate grout was tested with deionized water, 100% acetone, 100% ethylene glycol, real-site paint waste, real-site refinery waste, and reagent grade xylene. This grout was not tested with all ten of the planned chemicals because of its disappointingly high permeability. Two or more sodium silicate samples were tested with each of the above listed chemicals.

∘ Permeability Test of Sodium Silicate With Deionized Water

No sodium silicate samples were tested with water alone. However, all the samples were tested with water prior to the introduction of the chemicals, some of them with more than 8 pore volumes of flow with water.

As shown in Figures 68 through 74, the curves with water behaved very consistently. The samples quickly reached their equilibrium permeability; and with only minor variations maintained that rate of flow until the introduction of the chemical. Sample SS-11 is an example of this. It started out at a permeability of 4.7 x 10^{-5} cm/sec, reached 5.5 x 10^{-5} cm/sec after 2.5 pore volumes of flow, and maintained this until an accumulated flow of 10.8 pore volumes with water, at which point the ethylene glycol was introduced into the sample.

Averaging the equilibrium and final permeability values of 11 sodium silicate grout samples with water, a mean value of 5 x 10^{-5} cm/sec was obtained, a very high value for cutoff construction. The median value of permeability was 6 x 10^{-5} cm/sec. The consistency of the permeabilities of the sodium silicate samples was only fair, with a few samples yielding permeabilities in the range of 8 x 10^{-6} cm/sec, and one sample 2 x 10^{-7} cm/sec. There was no explanation why this occurred.

It should be noted that the data indicates that some of the samples were tested with only 0.3 or 0.4 pore volume of flow of water before the introduction of the chemicals. This is incorrect, as these samples were early test samples of the program, and were permeated with water without adequate records.

- Permeability Test of Sodium Silicate Grout with 100% Acetone

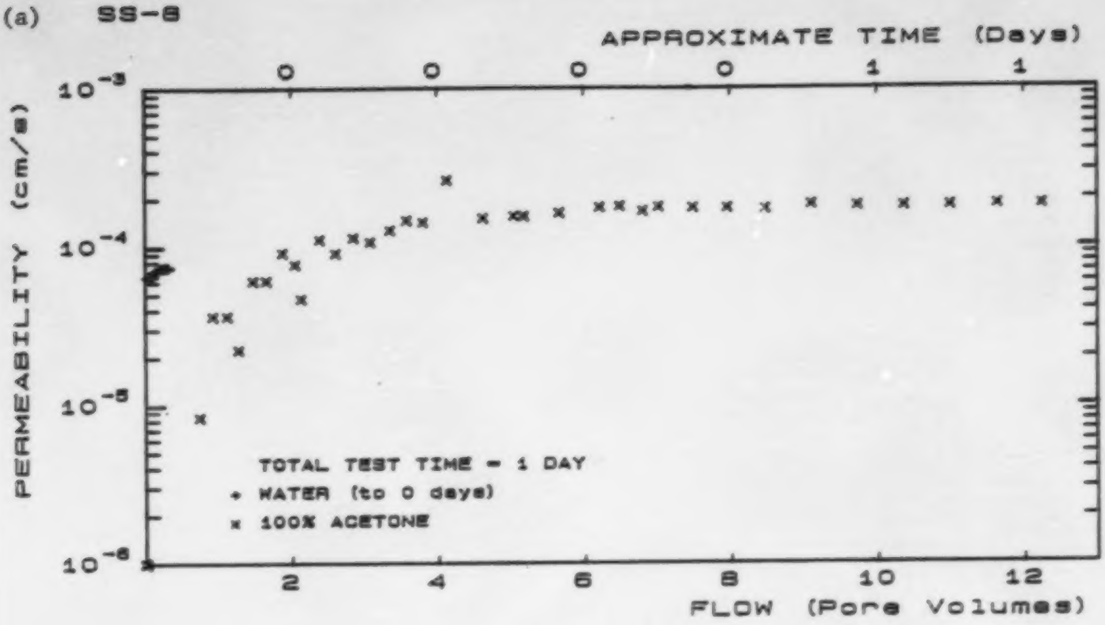
Two sodium silicate grout samples, SS-8 and SS-14, were tested with 100% acetone. The samples were 84 and 68 mm thick, respectively, and their diameters were 75 mm. Figure 68 shows the permeability versus pore volume flow plots for the two samples.

Preceding the introduction of acetone, the samples were saturated with water. The water permeation for sample SS-8 was accomplished at a net confining pressure of approximately 131 kPa (19 psi), a headpressure of approximately 6.9 kPa (1 psi), and a backpressure of zero. The gradient was approximately 8. The headpressure was achieved by the weight of the column of water in the headpipe without extra pressure. The permeability of the sample was approximately 6.6 x 10^{-5} cm/sec at the start of the test and rose slightly to a final equilibrium of 7.5 x 10^{-5} cm/sec with water. The total amount of flow of water was 0.32 pore volume. Deionized water was permeated through sample SS-14 at a headpressure of approximately 6.9 kPa (1 psi). The net confining pressure was approximately 235 kPa (34 psi) and the gradient was approximately 10. The sample was tested to 8.1 pore volumes of flow with water. The permeability versus pore volume flow curve was level. The equilibrium value of the permeability at the end of the test with water was 6.1 x 10^{-5} cm/sec.

Acetone was introduced into sample SS-8 under the same head conditions and at the same gradient as were used with water; however, the net confining pressure was dropped to approximately 34.5 kPa (5 psi). With the introduction of acetone, the permeability of the sample decreased by almost two orders of magnitude to a value of 8.5 x 10^{-6} cm/sec, then rose gradually to an equilibrium permeability of 1.8 x 10^{-4} cm/sec, after a cumulative flow of 6.2 pore volumes of acetone. The sample maintained this value of permeability for the remainder of the test, to a total flow of 12.3 pore volumes of acetone. The acetone was introduced into sample SS-14 with pressure and gradient conditions identical to those used with water. With the acetone the permeability of the sample gradually rose and, after a pore volume flow of 4.7 of acetone, it reached an equilibrium permeability of 2 x 10^{-4} cm/sec. The permeability of the sample remained practically at the same level to the end of the test which was terminated after a total of 8.2 pore volumes of acetone.

As shown in Figure 68, both sodium silicate samples showed slight increases in their permeabilities with acetone, amounting to a net change of approximately 0.5 to 0.6 order of magnitude. Their permeability versus pore volume flow curves with acetone appeared to be similar and both curves rose to a smooth and level final segment.

(a)



(b)

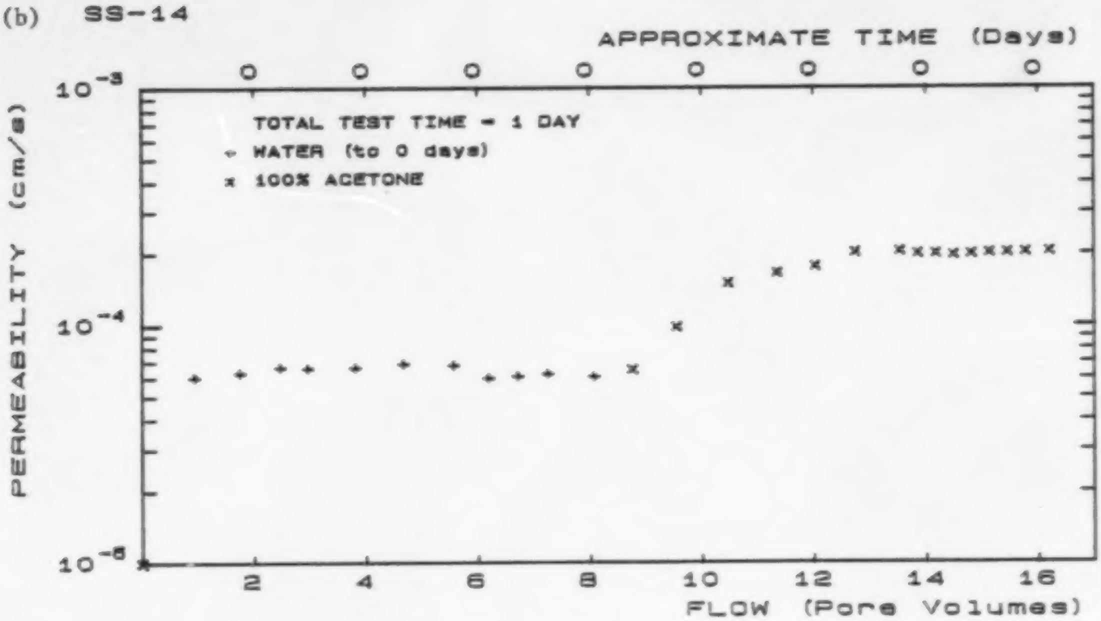


Figure 68. Permeability versus volume of flow of water and 100% acetone through sodium silicate grout. (a) Plot for sample SS-8. (b) Plot for sample SS-14.

◦ Permeability Test of Sodium Silicate Grout With 100% Ethylene Glycol

Two sodium silicate grout samples, SS-11 and SS-13, were tested with 100% ethylene glycol. Their thicknesses were 76 and 73 mm, respectively, and both were 75 mm in diameter. Figure 69 shows the permeability versus pore volume flow plots for the two samples.

Both samples were first saturated with water, which was accomplished in a falling-head type permeability apparatus with a headpressure of approximately 6.9 kPa (1 psi). During the test with water, both samples had a net confining pressure of approximately 235 kPa (34 psi) and a hydraulic gradient of 9. Sample SS-11 exhibited a permeability versus flow curve which was quite uniform and level, and had an equilibrium permeability of 6 x 10^{-5} cm/sec and a total flow of 10.9 pore volumes of water. For sample SS-13, the test with water resulted in a slightly downward sloping permeability versus flow curve as shown in Figure 69. The average permeability value at the end of its test on water was 6.1 x 10^{-5} cm/sec.

Ethylene glycol was introduced into sample SS-11 essentially under the same pressure conditions as were used with water, except that the net confining pressure was reduced to 166 kPa (24 psi). Upon the introduction of ethylene glycol, the sample exhibited a sharp decrease in its permeability. With an accumulated flow of 1.4 pore volumes of ethylene glycol, the permeability dropped to 3.9 x 10^{-6} cm/sec. From there, the permeability continued to decrease very gradually and bottomed out at 2.2 x 10^{-6} cm/sec at an accumulated 6.1 pore volumes of flow of ethylene glycol. The permeability versus flow curve finally came to equilibrium at a permeability of 3 x 10^{-6} cm/sec after a total of 8 pore volumes of flow with ethylene glycol.

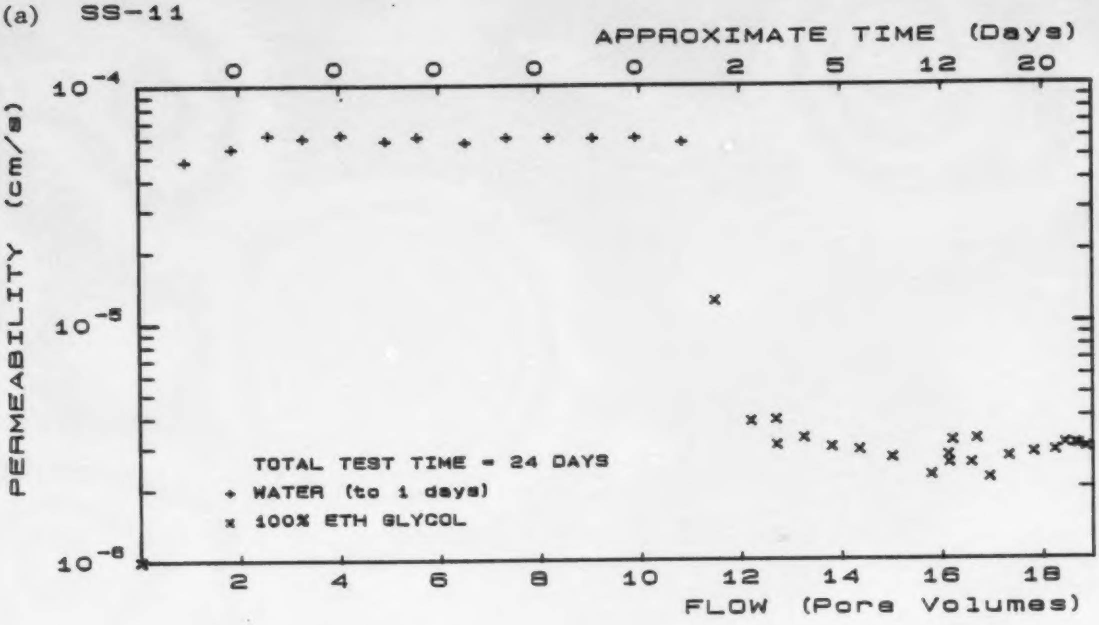
Ethylene glycol was introduced into sample SS-13 at a headpressure of approximately 28 kPa (4 psi), a tailpressure of zero, and a net confining pressure of approximately 162 kPa (23.5 psi). A gradient of 39 was used. As with sample SS-11, the introduction of ethylene glycol caused a sharp reduction in the permeability of sample SS-13, which dropped to 4.1 x 10^{-6} cm/sec with only 1.5 pore volumes of flow with ethylene glycol. With continued flow, the sample came to an equilibrium permeability of 3.8 x 10^{-6} cm/sec at a total pore volume flow of 15.4 with ethylene glycol.

On examining the two permeability versus flow curves for sodium silicate grouts on ethylene glycol, one observes that the curves are very consistent. Both samples on ethylene glycol showed an approximately 1.3 orders of magnitude drop in permeability from that measured with water. Also, both samples ended with approximately the same final equilibrium permeability, the values being 3 and 3.8 x 10^{-6} cm/sec, respectively.

◦ Permeability Test of Sodium Silicate Grout With Real-Site Paint Waste

Three sodium silicate grout samples, SS-3B, SS-5B, and SS-10, were tested with real-site paint waste. Their respective thicknesses were 33, 33, and 91 mm. All three were 75 mm in diameter. Figures 70 and 71 show the permeability versus pore volume flow plots for the three samples.

(a) SS-11



(b) SS-13

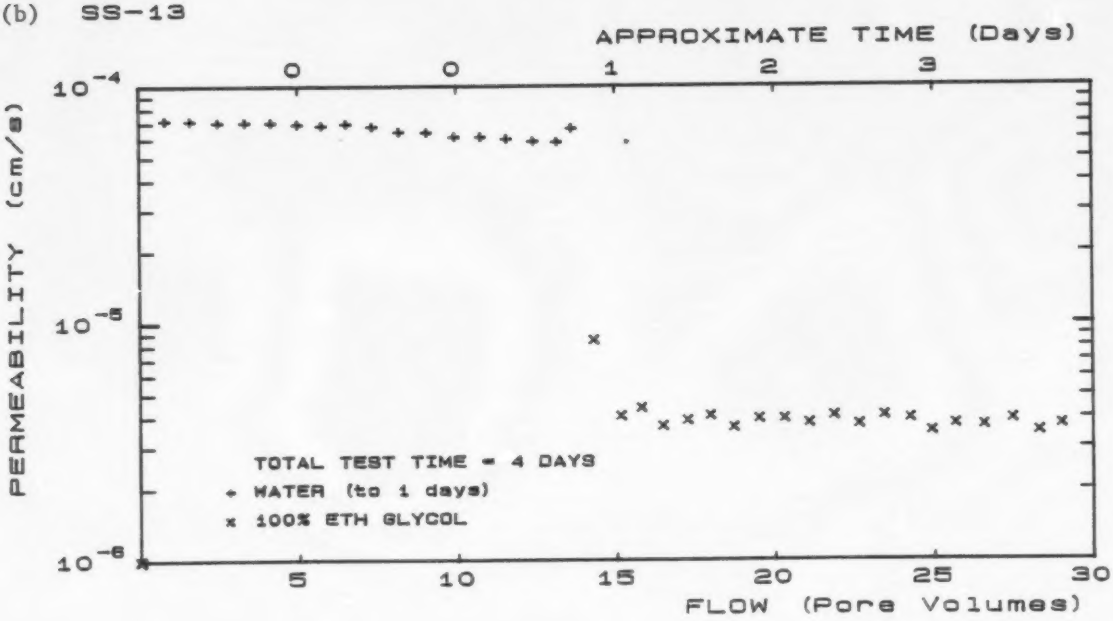


Figure 69. Permeability versus volume of flow of water and 100% ethylene glycol through sodium silicate grout. (a) Plot for sample SS-11. (b) Plot for sample SS-13.

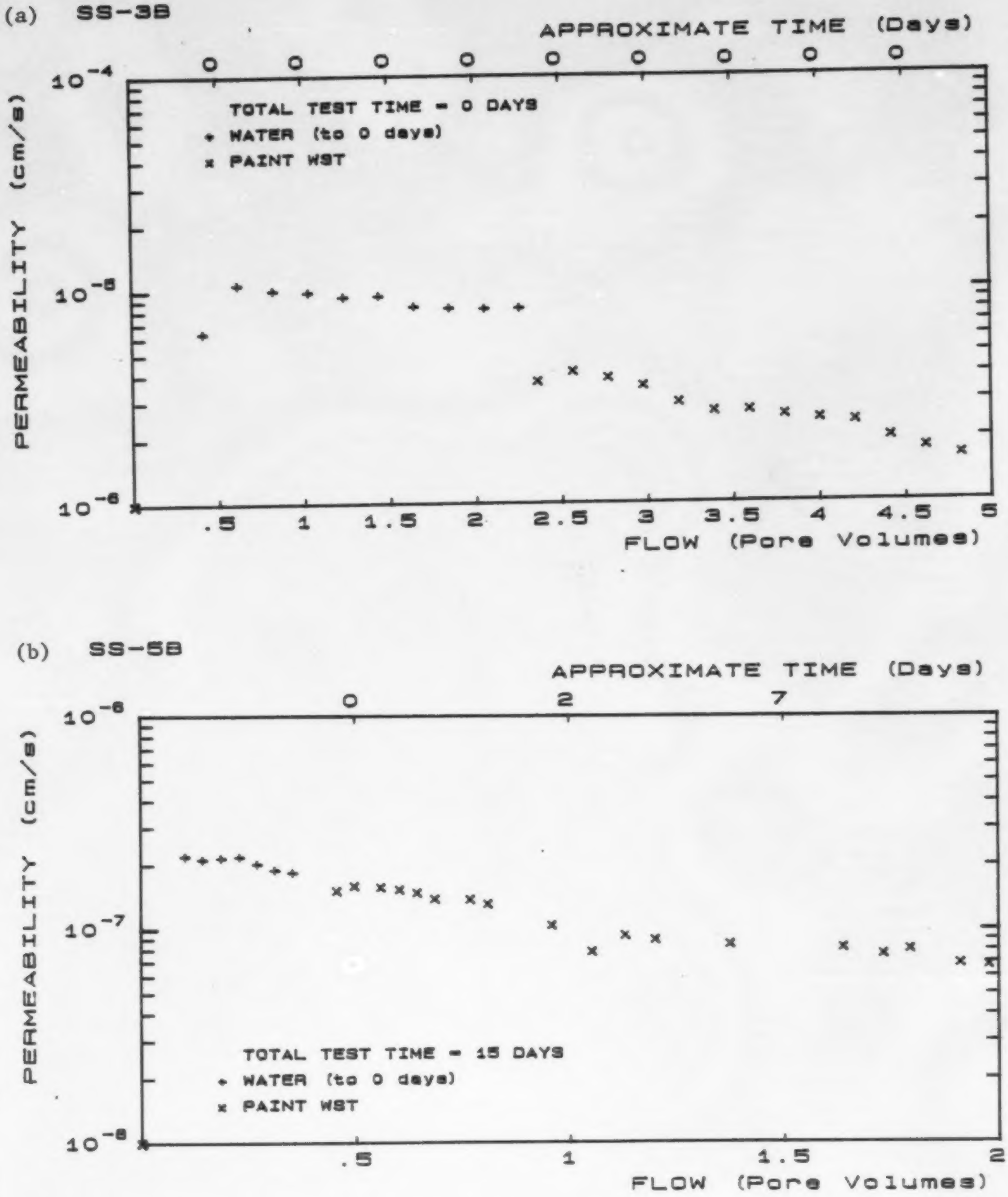


Figure 70. Permeability versus volume of flow of water and real-site paint waste through sodium silicate grout. (a) Plot for sample SS-3B. (b) Plot for sample SS-5B.

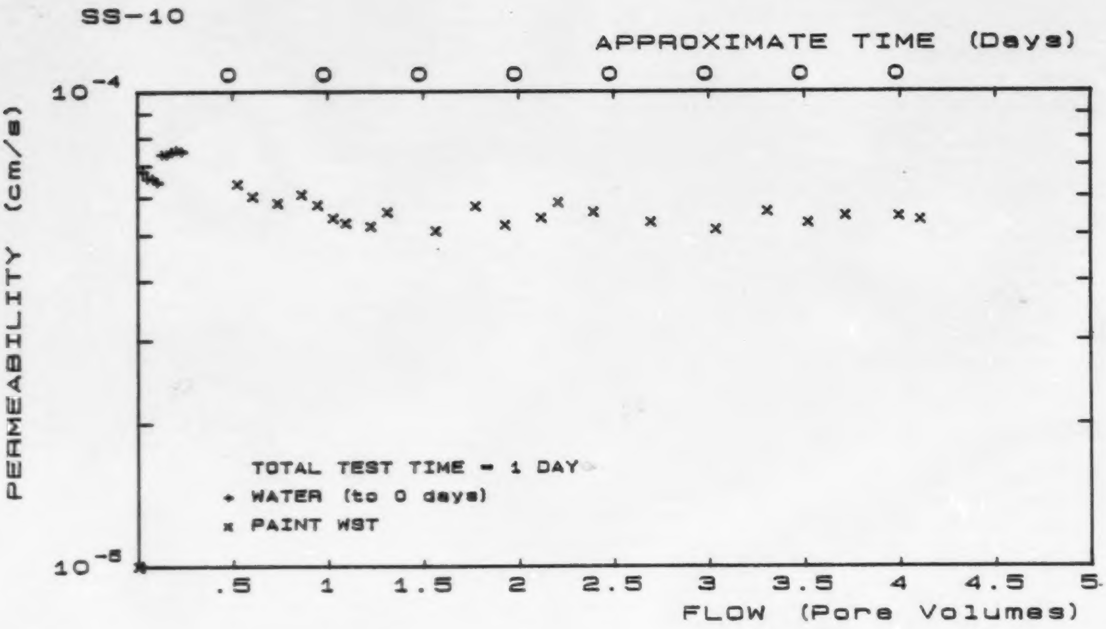


Figure 71. Permeability versus volume of flow of water and real-site paint waste through sodium silicate grout sample SS-10.

Preceding the introduction of paint waste, the three samples were saturated with water. The water permeation of all three samples was accomplished at a net confining pressure of 138 kPa (20 psi) and a backpressure of zero. A headpressure of 138 kPa (20 psi) was used for samples SS-3B and SS-5B, while sample SS-10 was permeated in a falling-head permeability apparatus with an average headpressure of 6.9 kPa (1 psi). Correspondingly, the gradients at which the permeation occurred were approximately 426 for samples SS-3B and SS-5B, and 8 for sample SS-10. The permeation with water resulted in a fairly level end segment for the permeability versus pore volume flow curve of sample SS-3B. The equilibrium permeability was 8.4 x 10^{-6} cm/sec with a total flow of 2.3 pore volumes of water. For sample SS-5B, the permeability versus flow curve was fairly uniform with a slightly decreasing permeability with flow. The final permeability with water was 1.9 x 10^{-7} cm/sec, after a pore volume flow of 0.4. The permeability versus flow curve for sample SS-10 became fairly level at the end of its test with water, with the permeability equilibrating at 7.5 x 10^{-5} cm/sec after a pore volume flow of 0.23. As it can be observed, all three samples gave a different equilibrium permeability with water.

The paint waste was introduced into sample SS-3B at essentially the same pressure and gradient conditions as were used with water. After the introduction of paint waste, the permeability of the sample decreased from 8.4 x 10^{-6} cm/sec to 4 x 10^{-6} cm/sec within 0.2 pore volumes of flow with paint waste. With increasing flow, the permeability of the sample was found to have decreased continuously until the termination of the test. It reached a final permeability of 2.7 x 10^{-6} cm/sec after a flow of 1.34 pore volumes of paint waste.

The paint waste was introduced into sample SS-5B at pressure and gradient conditions that were identical to the ones used with water; however, in the second half of the test the headpressure was reduced to approximately 6.9 kPa (1 psi), the gradient to 21, while the net confining pressure was increased to 207 kPa (30 psi). The introduction of paint waste caused little initial change in the permeability of the sample and, with continued flow, the permeability of the sample decreased very gradually. The test was terminated after 1.6 pore volumes of paint waste flow, by which time the permeability had dropped to 6.9 x 10^{-8} cm/sec.

The paint waste was introduced into sample SS-10 at essentially the same pressure and gradient conditions as were used with water, except that the net confining pressure was increased first to 200 kPa (29 psi) and then to 235 kPa (34 psi). With paint waste percolating through the sample, the permeability initially dropped from 7.5 x 10^{-5} cm/sec to 6.5 x 10^{-5} cm/sec, then continued its gradual downward trend with increasing flow. The permeability of the sample bottomed out after 1.6 pore volumes of paint waste flow at a value of 5.1 x 10^{-5} cm/sec. Following this period, the permeability of the sample recovered somewhat and came to an equilibrium at 5.5 x 10^{-5} cm/sec, after an accumulated 4.5 pore volumes of paint waste flow.

As pointed out before, all three samples give different baseline permeabilities with water. The reasons for this are unknown. With paint waste, the samples generally exhibited little change. All three permeability curves show moderately decreasing permeability with paint waste flow. The reasons for this were visible clumps of microorganisms that grew in the waste and are believed to have plugged the sample voids. This effect was not as pronounced with paint waste as it was with refinery waste.

- Permeability Test of Sodium Silicate Grout With Real-Site Refinery Waste

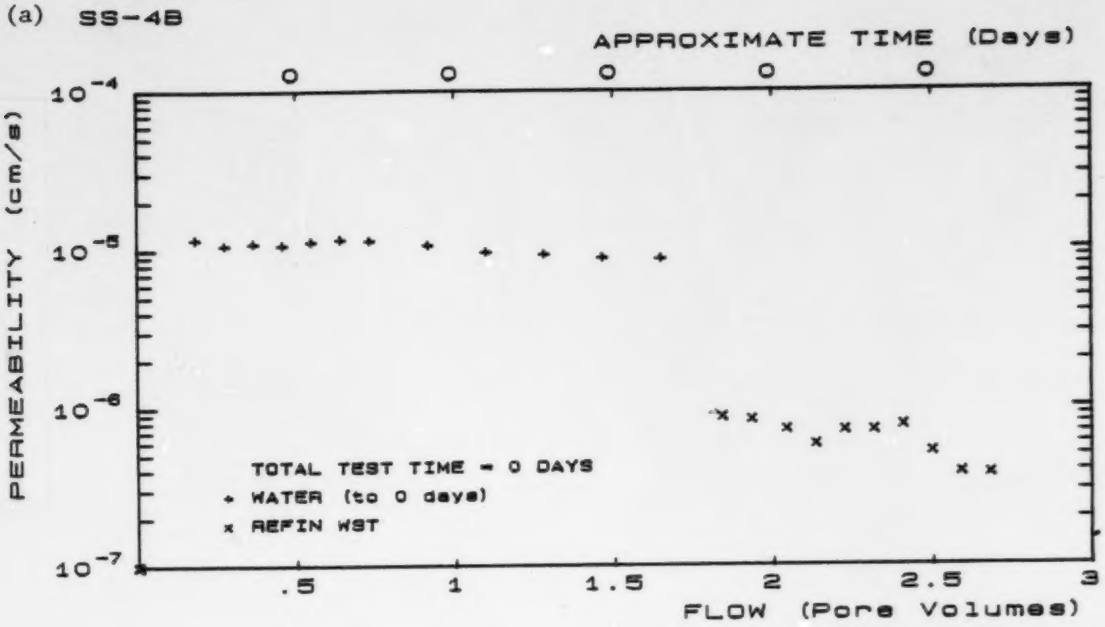
Three sodium silicate grout samples, SS-4B, SS-6B and SS-9, were tested with real-site refinery waste. Their thicknesses were 37, 32, and 91 mm, respectively, and all three were 75 mm in diameter. Figures 72 and 73 show the permeability versus pore volume flow plots for the three samples.

Before refinery waste was introduced into the samples, they were saturated with water. Samples SS-4B and SS-6B were permeated with water at a headpressure of 69 kPa (10 psi), a backpressure of zero, and a net confining pressure of 173 kPa (25 psi). The test gradients were 190 and 220, respectively, for samples SS-4B and SS-6B. Sample SS-9 was permeated with water in a falling-head test apparatus with a headpressure of approximately 6.9 kPa (1 psi), a tailpressure of zero, and a net confining pressure of 131 kPa (19 psi). The test gradient was approximately 8. Sample SS-4B exhibited a fairly uniform permeability versus flow curve with water and equilibrated at a permeability of 9.2×10^{-6} cm/sec after a flow of 1.7 pore volumes. Sample SS-6B exhibited a gradually decreasing curve with water resulting in a final permeability of 3.1×10^{-6} cm/sec after a pore volume flow of 1.2 on water. Sample SS-9 also had a slightly downward sloping permeability versus flow curve that came to an equilibrium permeability value of 7.8×10^{-5} cm/sec after a pore volume flow of 0.26 with water.

The refinery waste was introduced into sample SS-4B at a headpressure of 138 kPa (20 psi), a tailpressure of zero, and a net confining pressure of 138 kPa (20 psi). The test gradient was 380. The headpressure was increased later in the test to 173 kPa (25 psi), which in turn increased the net confining pressure to 155 kPa (22.5 psi) and the gradient to 475. The introduction of refinery waste into the sample caused a sharp downturn in its permeability to a level of 8.9×10^{-7} cm/sec with an accumulated 0.2 pore volume flow of refinery waste. With continued flow the permeability kept on decreasing, and at the end of the test it reached a low value of 3.9×10^{-7} cm/sec. It is believed by these writers that this sample was not tested long enough and, had it been, its permeability would have dropped further.

The refinery waste was introduced into sample SS-6B at various head and confining pressure conditions and gradients. The test started out at a headpressure of 138 kPa (20 psi), a tailpressure of 0, a net confining pressure of 138 kPa (20 psi), and a gradient of 439. The headpressure was later increased to 173 kPa (25 psi) and then dropped to 14 kPa (2 psi). Correspondingly, the net confining pressure and gradient were first raised to 155 kPa (22.5 psi) and 549, then dropped to 235 kPa (34 psi) and 44, respectively. As shown in Figure 72(b), the introduction of refinery waste caused a moderate drop in the permeability of this sample, from 3.1×10^{-6} cm/sec to 5.6×10^{-7} cm/sec, with only 0.3 pore volume flow of refinery waste. Thence, the permeability of the sample decreased continuously until it leveled off temporarily at a permeability of approximately 6.6×10^{-8} cm/sec after a flow

(a) SS-4B



(b) SS-6B

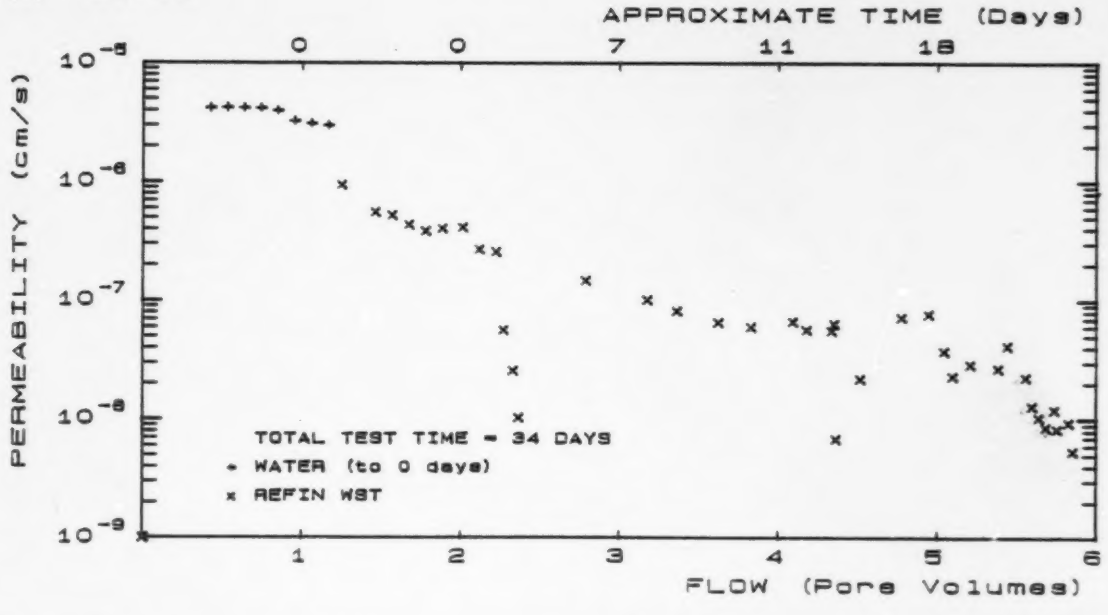


Figure 72. Permeability versus volume of flow of water and real-site refinery waste through sodium silicate grout. (a) Plot for sample SS-4B. (b) Plot for sample SS-6B.

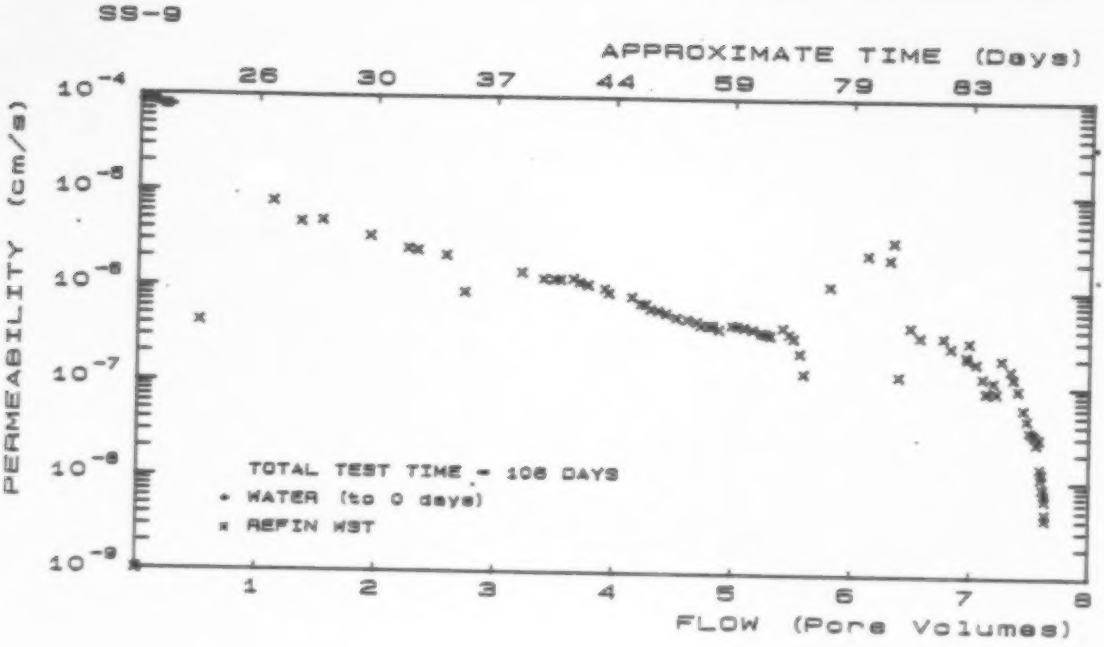


Figure 73. Permeability versus volume of flow of water and real-site refinery waste through sodium silicate grout sample SS-9.

of 2.5 pore volumes of refinery waste. With continued flow, the sample exhibited further decreases in its permeability which, at the end of the test and after 4.7 pore volumes of flow of refinery waste, reached a value of 5.5 x 10^{-9} cm/sec.

The refinery waste was introduced into sample SS-9 at essentially the same pressure conditions as were used with the water. For the second half of the test the headpressure was increased to 21 kPa (3 psi), the net confining pressure to 231 kPa (33.5 psi), and the gradient to 23. With the introduction of refinery waste, the permeability of the sample dropped to 4.8 x 10^{-6} cm/sec after 1.1 pore volumes of flow of refinery waste. During continued flow, the permeability kept on decreasing and reached a value of 2 x 10^{-7} cm/sec after 7.0 pore volumes of flow of refinery waste. At that point the permeability decreased sharply. In fact, the permeability curve seems to have come to a vertical asymptote, and the sample approached a practically impervious state. The final reading in the test gave a permeability of 4.9 x 10^{-9} cm/sec after 7.4 pore volumes of flow of refinery waste.

In summary, all three samples had similar permeability versus pore volume flow curves, except that sample SS-4B was probably not tested long enough with refinery waste.

In comparing the three test curves, they all exhibited a fairly uniform and slightly decreasing permeability with water flow. With the introduction of refinery waste, the samples underwent an initial sharp drop in their permeabilities that was followed by a gradually decreasing permeability with flow. Toward the end of the tests of samples SS-6B and SS-9, the permeability versus flow curve turned sharply down, indicating a quickly developing blockage of flow inside these samples. This is attributed to the microorganisms that grew and were visible in the inflow lines leading to the samples. It is postulated that once these organisms got inside the samples, they blocked the pore openings and thus decreased the permeability of the samples.

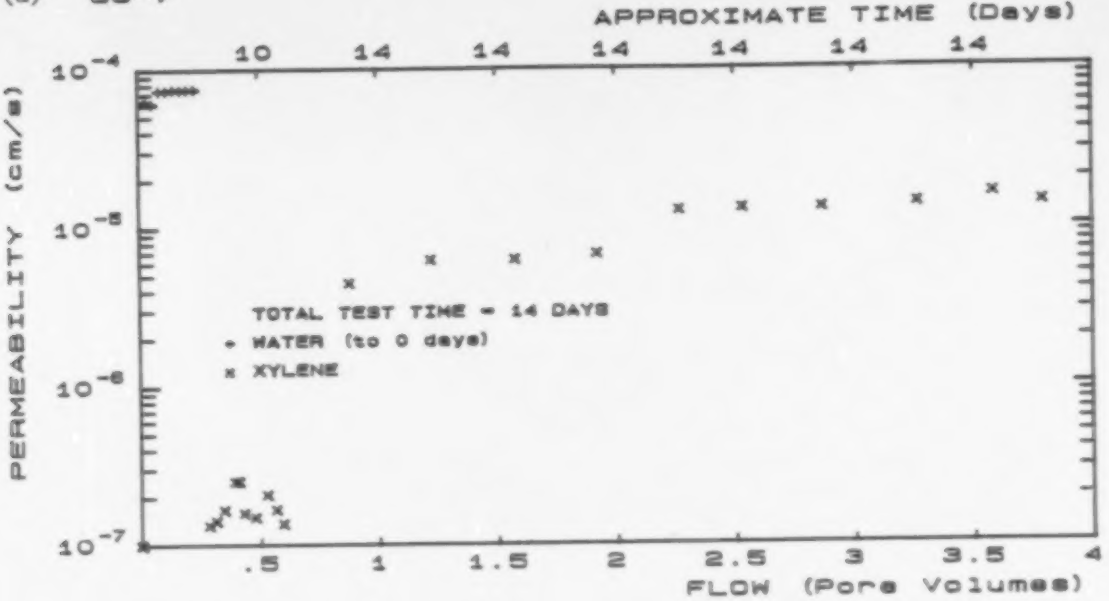
- Permeability Test of Sodium Silicate Grout With Xylene

The two sodium silicate grout samples tested with xylene were designated as SS-7 and SS-12. The first sample had a thickness of 80 mm, the second 78 mm. Both had a diameter of 75 mm. Their permeability versus pore volume flow plots are shown in Figure 74.

Prior to the introduction of xylene, both sodium silicate samples were saturated with water. Saturation of the samples was achieved by forcing water to flow through the samples at a headpressure of 6.9 kPa (1 psi), a backpressure of zero, and a gradient of 9. The net confining pressures used were 131 kPa (19 psi) for sample SS-7 and 97 kPa (14 psi) for sample SS-12. Both samples exhibited very consistent and level permeability versus flow curves with water. Sample SS-7 achieved its equilibrium permeability at 7.5 x 10^{-5} cm/sec with a flow of 0.23 pore volume of water. Sample SS-12 was tested with water for the extended flow range of 18.5 pore volumes and resulted in a terminal equilibrium permeability of 7 x 10^{-5} cm/sec.

Sample SS-7 was tested with xylene in a falling-head permeability appara-

(a) SS-7



(b) SS-12

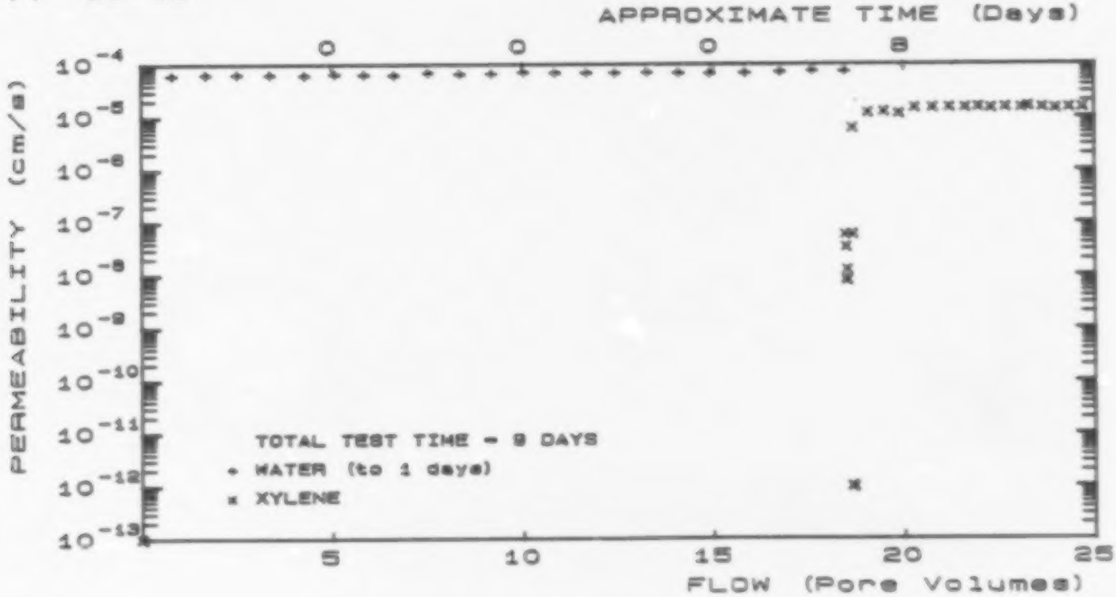


Figure 74. Permeability versus volume of flow of water and xylene through sodium silicate grout. (a) Plot for sample SS-7. (b) Plot for sample SS-12.

tus with an approximate headpressure of 6.9 kPa (1 psi), a tailpressure of zero, and a net confining pressure of 200 kPa (29 psi). The test was run at an approximate gradient of 9. The introduction of xylene caused the permeability of the sample to drop to 1.4 x 10^{-7} cm/sec. The permeability stayed around this value over 0.36 pore volume of flow, then it suddenly rose and leveled off at a permeability of 6.5 x 10^{-6} cm/sec after an accumulated flow of 1.0 pore volume with xylene. Following a pore volume flow of 2.0 with xylene, the permeability of the sample rose further to a value of 1.3 x 10^{-5} cm/sec, and finally leveled off at a permeability value of 1.5 x 10^{-5} cm/sec with an accumulated flow of 3.6 pore volumes of xylene.

The xylene was introduced into sample SS-12 at a headpressure of 21 kPa (3 psi). Later in the test the headpressure was increased to 42 kPa (6 psi). The tailpressure was set at zero. The net confining pressure started out at 231 kPa (33.5) and was decreased to 221 kPa (32 psi) with the above described increase in headpressure. The gradient used was 27 at the beginning and was later increased to 54. As in sample SS-7, the introduction of xylene into sample SS-12 caused a large decrease in its permeability. The permeability bottomed out at 8 x 10^{-9} cm/sec after only 0.1 pore volume of flow of xylene. However, after an accumulated flow of 0.5 pore volume of xylene, the permeability increased to 1.2 x 10^{-5} cm/sec, stayed there for an additional flow of 0.8 pore volumes, then increased to 1.5 x 10^{-5} cm/sec and stayed there until the end of the test, which was terminated at an accumulated flow of 6.5 pore volumes of xylene.

In comparing the two curves for sodium silicate grout on xylene, one may observe that they both exhibited uniform high permeabilities with water, sharp drops with the introduction of xylene, which were followed by increases in permeabilities to practically identical final levels of 1.5 x 10^{-5} cm/sec. In summary, there were no discernable harmful effects of xylene on the sodium silicate grout, in fact, the final permeability values of the samples with xylene were lower than those with water.

- Analysis of Permeability Test Results For Sodium Silicate Grout

The sodium silicate grout was permeated with five chemicals to determine if any changes would take place in its permeability with chemical flow. The bar chart shown in Figure 75 summarizes the results of these permeability tests (see the section titled Analysis of Permeability Test Results for Acrylate Grout for the interpretation of the notation in this chart).

As shown, the sodium silicate grout was relatively pervious with water, and the baseline permeabilities of the grout samples varied between 5.8 x 10^{-6} cm/sec and 7.3 x 10^{-5} cm/sec. Because of its high permeability with water, this grout mix will probably not be used in hazardous waste barrier construction. However, the grout was considered to be relatively resistant to chemicals and therefore it was of some interest to find the general trend of its permeability with the various chemicals. Consequently, the grout was tested with five chemicals.

The permeability of the sodium silicate grout increased with reagent grade acetone. This rise was less than 0.5 order of magnitude. With 100%

ethylene glycol, real-site refinery waste, and reagent grade xylene the permeability of the grout actually decreased from its baseline value with water. This decrease was approximately 1.3 orders of magnitude for the samples with ethylene glycol and 1.75 orders of magnitude for samples with refinery waste. The permeability decreases of the samples with xylene and paint waste were small and negligible, respectively.

While the samples were tested with paint waste and refinery waste, biological growths were seen growing in the feed lines, especially the ones containing the refinery waste. It is assumed that once these growths reached the grout samples, they started to plug the voids in the grout and thereby started to gradually decrease the permeability of the samples.

In summary, the sodium silicate grout samples had relatively high permeabilities with deionized water. In contrast, the chemicals had practically no detrimental effects on the grout, and in three cases they, or the biological growths, even caused a decrease in the permeability of the test samples.

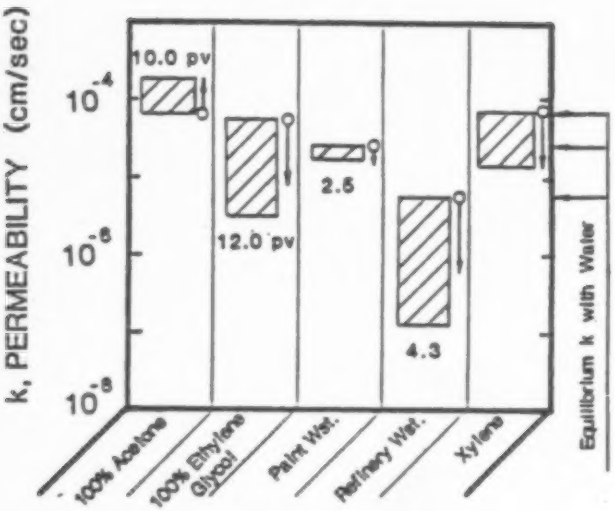


Figure 75. Permeability of sodium silicate grout with various chemicals.

Permeability Tests of Glyoxal-Modified Sodium Silicate Grout

As discussed in the previous section, the sodium silicate grout was a disappointment because of its high permeability with water. Since sodium silicate is a fairly inert material and its permeability may not be affected by chemicals, an attempt was made to improve its permeability by the addition of glyoxal.

The glyoxal-modified sodium silicate grout was easy to mix and inject into the fine brown sand used. The grout samples obtained were very hard and brown in color. They were 75 mm in diameter and between 60 and 80 mm in thickness.

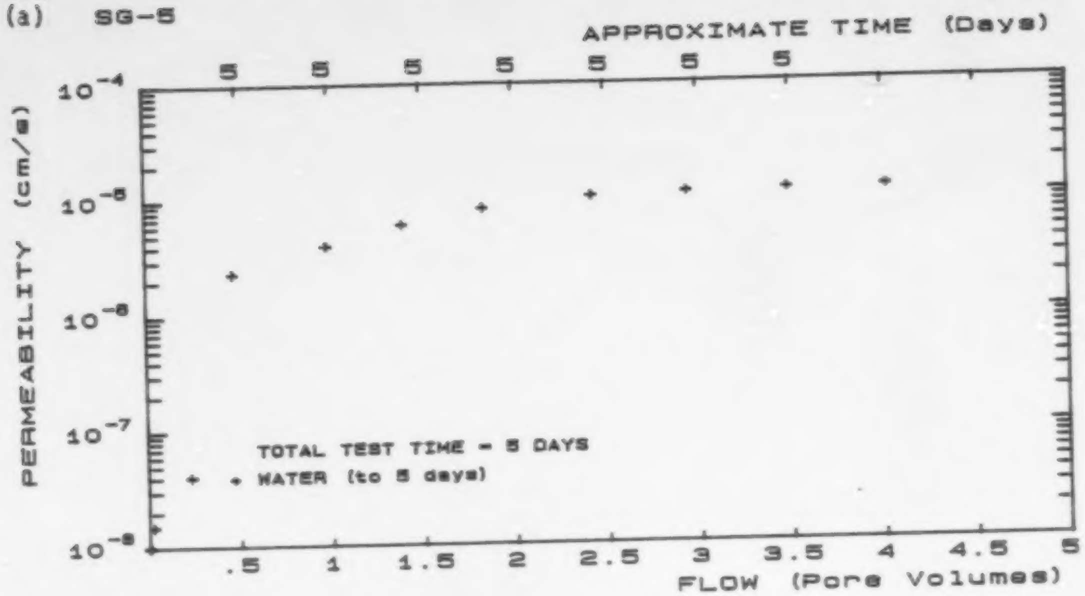
All grout samples were permeated with deionized water prior to their testing with chemicals. Also, samples SG-5 and SG-6 were tested continuously with water, sample SG-6 to a pore volume flow of 18. Their average baseline permeability with water was 1.9 x 10^{-5} cm/sec. This was a high permeability, and the grout was a disappointment.

The following sections present the test data and results for the glyoxal-modified sodium silicate grout samples that were permeated with deionized water and various chemicals, specifically, 20% solution of cupric sulfate, 25% solution of sodium hydroxide, and reagent grade xylene.

- Permeability Test of Glyoxal-Modified Sodium Silicate Grout With Deionized Water

All glyoxal-modified sodium silicate grout samples were first permeated with water in order to saturate them before their testing with chemicals. They were permeated with water until they reached equilibrium, which on the average occurred after a pore volume flow of 2.4. At this flow the average permeability of the 8 samples tested was 1.9 x 10^{-5} cm/sec, a high permeability.

Two grout samples, SG-5 and SG-6, were tested with water alone. Figure 76 shows the permeability versus pore volume flow graphs obtained for these samples. They were tested at constant hydraulic gradients of 23.5 and 22.7, respectively. Sample SG-5 started out at a low permeability. However, its permeability started to rise, first quickly and then more gradually, until it reached an equilibrium of 1.2 x 10^{-5} cm/sec at 3.5 pore volumes of flow. Its testing was terminated after 4.1 pore volumes of flow. Sample SG-6 had an initial permeability of 1.6 x 10^{-5} cm/sec with water. This rose to 1.9 x 10^{-5} cm/sec after 2.8 pore volumes of flow and stayed at that level until 7.0 pore volumes. At that point the permeability jumped to 3.9 x 10^{-5} cm/sec, then hesitated before it slowly climed to its final equilibrium of 4.7 x 10^{-5} cm/sec at 15.4 pore volumes of flow. It is worth noting that one other sample, SG-4, also had a small jump in its permeability after 5 pore volumes of flow with water. Its permeability rose from 8 x 10^{-6} cm/sec to 2.5 x 10^{-5} cm/sec. Since both jumps in permeability occurred after 5 pore volumes of flow, and none of the other samples were tested to that accumulated flow with water, the equilibrium permeability of this grout with water is in question, however, it most certainly is between 1 x 10^{-5} and 5 x 10^{-5} cm/sec,



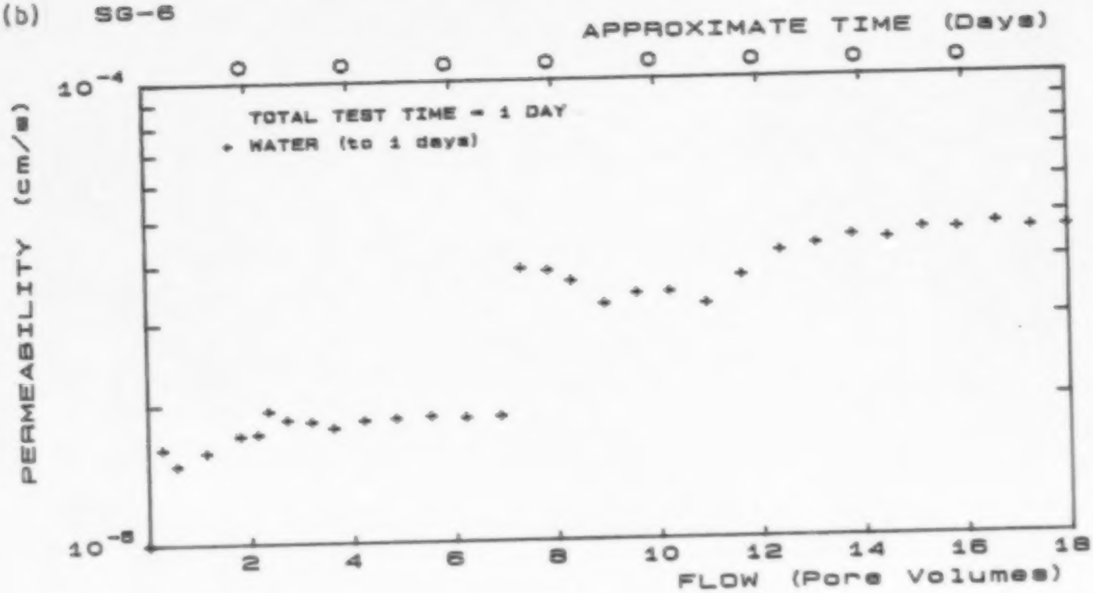


Figure 76. Permeability versus volume of flow of water through glyoxal-modified sodium silicate grout. (a) Plot for sample SG-5. (b) Plot for sample SG-6.

a high permeability in either case.

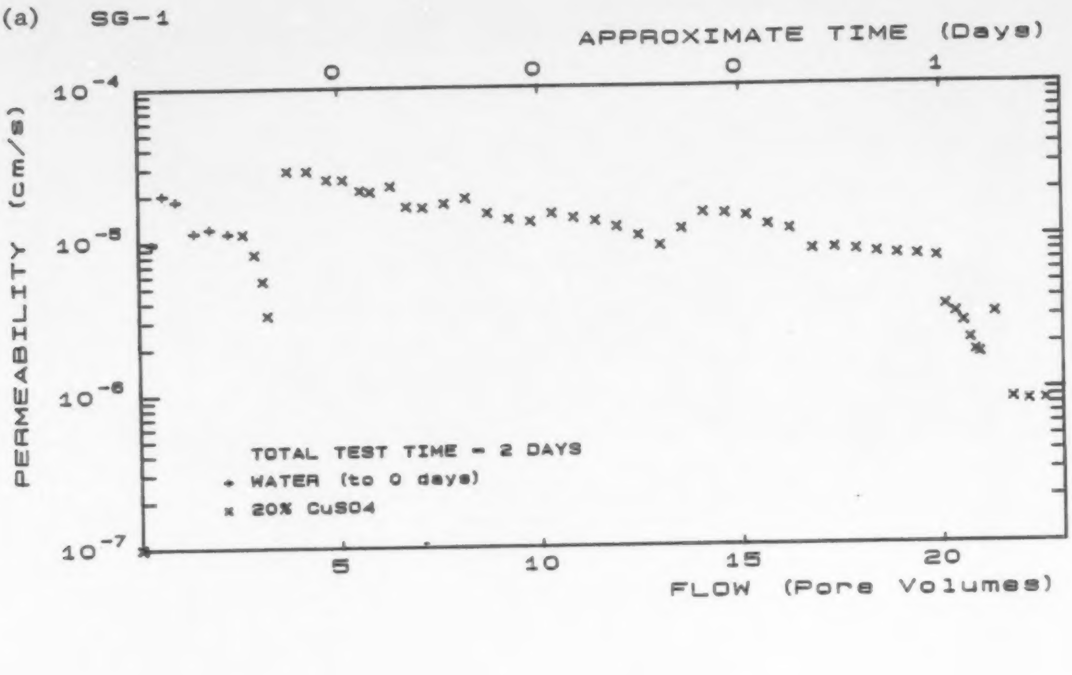
- Glyoxal-Modified Sodium Silicate Grout Samples Permeated With a 20% Cupric Sulfate Solution

Two glyoxal-modified sodium silicate grout samples designated SG-1 and SG-2, were tested with a 20% solution of cupric sulfate in water. Each sample had a thickness of 63 mm and a diameter of 75 mm. Figure 77 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SG-1 was permeated with water for 0.20 day with an accumulated flow of 2.3 pore volumes. Sample SG-2 was tested on water for 0.20 day with an accumulated flow of 2.8 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), a backpressure of zero, and a gradient of 22. The water permeability versus pore volume flow curves show little variation. The curve for SG-1 indicates an "average" equilibrium permeability of 1.5 x 10^{-5} cm/sec as compared to 1.7 x 10^{-5} cm/sec for SG-2. During the permeation process the effluent was discolored to a dark brown. This was most likely fine particles washed from the mason's sand and possibly some grout gel too. As time elapsed the effluent became lighter in color until it eventually turned clear.

A 20% cupric sulfate solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi). The backpressure was also unchanged at zero. However, due to an increase in driving head pressure (needed to overcome pressure caused by reaction of leachate and grouted soil) the gradient was increased to 55. Sample SG-1 was permeated with chemical for 1.1 days with an accumulated chemical flow of 17.9 pore volumes. Sample SG-2 was permeated with a 20% solution of cupric sulfate for 1.0 day with a sum chemical flow of 10.7 pore volumes. Permeability behavior was quite similar between the two samples.

Initially the samples were permeated with a gradient of 22. This translated into a driving head pressure of 13.8 kPa (2.0 psi) and a backpressure of zero. The driving headpressure, after approximately one pore volume of flow, had to be increased to 34.5 kPa (5.0 psi), yielding an increase in the gradient to 55, to overcome the pressure generated by the large amounts of gas being produced by the chemical leachate/grouted soil interaction and the effluent had a light brown tint. After increasing the gradient, a brownish clear gel formed on the sides of the effluent measuring buret and the effluent acquired a blue tint which is the normal color of cupric sulfate. The final equilibrium permeability (in spite of the scatter of the plotted points) was determined to be 8.6 x 10^{-7} cm/sec for SG-1 and 4.2 x 10^{-7} cm/sec for SG-2. These values are one to nearly two orders of magnitude lower than their water baseline permeabilities.



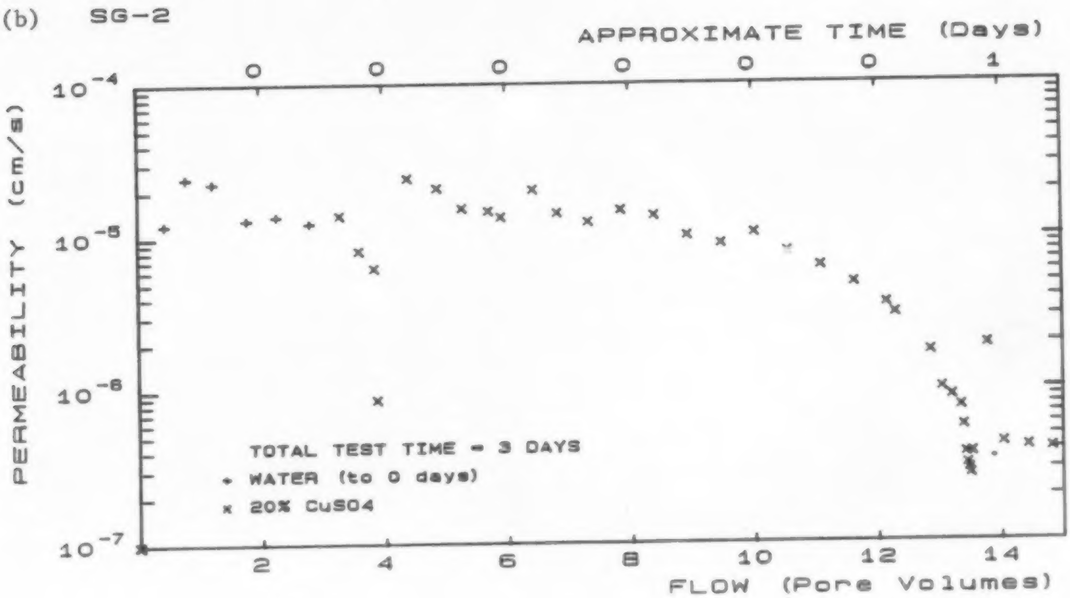


Figure 77. Permeability versus volume of flow of water and 20% cupric sulfate through glyoxal-modified sodium silicate grout. (a) Plot for sample SG-1. (b) Plot for sample SG-2.

- Glyoxal-Modified Sodium Silicate Grout Samples Permeated With a 25% Sodium Hydroxide Solution

Two glyoxal-modified sodium silicate grout samples, designated SG-7 and SG-8, were tested with a 25% solution of sodium hydroxide in water. Each sample had a diameter of 75 mm. Sample SG-7 had a thickness of 80 mm, and SG-8 a thickness of 75 mm. Figure 78 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SG-7 was permeated with water for 0.64 day with an accumulated flow of 1.8 pore volumes. Sample SG-8 was tested on water for 0.51 day with an accumulated flow of 3.2 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero. The gradients varied somewhat due to the difference in sample thicknesses. Sample SG-7 had a gradient of 18 and SG-8 a gradient of 17. The water permeability versus pore volume flow curves show over a fourfold variation. The curve for SG-7 indicates an equilibrium permeability of 5.4 x 10^{-6} cm/sec compared to 1.2 x 10^{-5} cm/sec for SG-8. During permeation the effluent became discolored. The dark brown tint faded after 2.0 pore volumes (1.1 being water and 0.9 being a 25% solution of sodium hydroxide in water) of flow for SG-7 and 3.5 pore volumes (0.5 being water and 3.0 being a 25% solution of sodium hydroxide in water) of flow for SG-8.

A 25% sodium hydroxide solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi), the backpressure at zero, and the gradient at 18 for SG-7 and 17 for SG-8. Sample SG-7 was permeated with chemical for 79.4 days with an accumulated chemical flow of 7.4 pore volumes. Sample SG-8 was permeated with a 25% solution of sodium hydroxide for 8.4 days with a sum chemical flow of 10.6 pore volumes. In one respect the chemical leachate/grouted soil reaction was similar for each of the samples but in other respects was quite different. The common tendency of the samples was to decrease in permeability. However, SG-8 did not maintain a low permeability for any great length of time. SG-7 was successful in retaining the leachate in such a way as to render the permeability immeasurable. Therefore, a permeability of 1.0 x 10^{-12} cm/sec was automatically assigned to this condition for purposes of graphical presentation. After approximately seven days the gradient was increased to 45 with the net confining pressure and backpressure kept at previous levels of 120.8 kPa (17.5 psi) and zero, respectively. SG-7 came to an equilibrium permeability of 1.8 x 10^{-7} cm/sec. This level was quite similar in magnitude to the permeability before the leachate ceased flowing.

Originally SG-8 had a baseline permeability roughly twice that of SG-7, nevertheless, this was inadequate to explain the significant difference between the equilibrium permeability of the two samples. Sample SG-7 had an equilibrium permeability of 1.8 x 10^{-7} cm/sec as compared to 1.5 x 10^{-5} cm/sec for SG-8, a variation of two orders of magnitude. One possible explanation is the "clogging" of SG-7 as evidenced by the extremely low (essentially immeasurable) value of permeability. However, SG-7 had a measurable permeability at a slightly higher gradient.

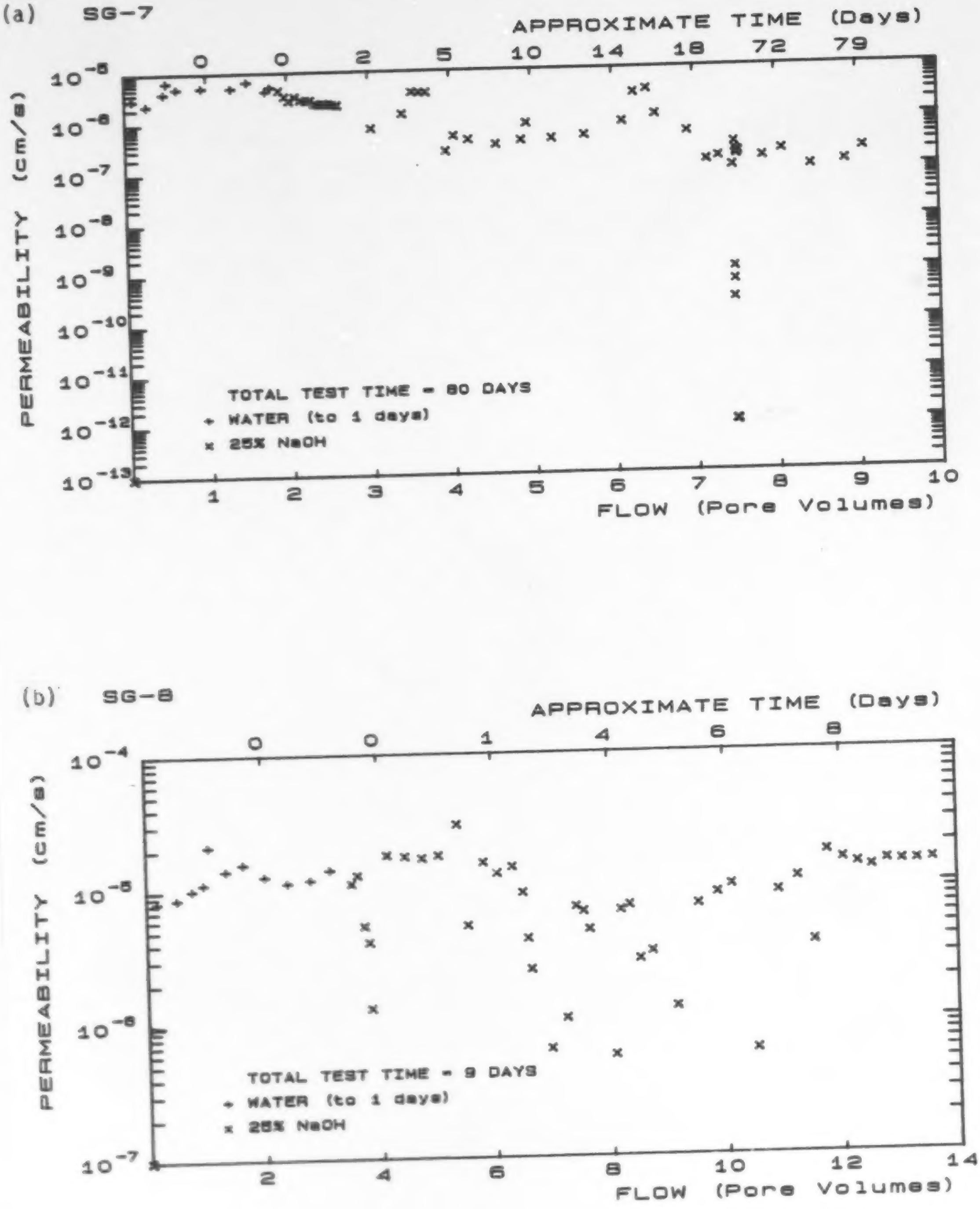


Figure 78. Permeability versus volume of flow of water and 25% sodium hydroxide through glyoxal-modified sodium silicate grout. (a) Plot for sample SG-7. (b) Plot for sample SG-8.

- Glyoxal-Modified Sodium Silicate Grout Samples Permeated With Reagent Grade Xylene

Two glyoxal-modified sodium silicate grout samples, designated SG-3 and SG-4, were tested with xylene. Each sample had a diameter of 75 mm. Sample SG-3 had a thickness of 61 mm and SG-4 a thickness of 62 mm. Figure 79 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SG-3 was permeated with water for 0.28 day with an accumulated flow of 4.5 pore volumes. Sample SG-4 was tested on water for 0.75 day with an accumulated flow of 10.5 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero. Both samples had gradients of 23. The water permeability versus pore volume flow curves for SG-3 and SG-4 show little variation in water baseline equilibrium permeabilities. The curve for SG-3 indicates a water equilibrium permeability of 1.7 x 10^{-5} cm/sec as compared to 2.6 x 10^{-5} cm/sec for SG-4. During permeation the effluent became discolored. The dark brownish tint indicated that fine sand particles, and possibly grout, were being washed from the sample. The effluent from SG-3 did not discolor until about 0.9 pore volume had percolated and did not clear until another 2.0 pore volumes passed. In comparison, the effluent from SG-4 became discolored at the beginning of permeation and continued for 4.0 pore volumes of flow. More material appeared to wash from sample SG-4 than from SG-3. This erosion could have increased the permeability of sample SG-4 and thus could explain the variation in permeabilities.

Reagent grade xylene (mixed isomers) was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi). The backpressure was maintained at zero. However, due to an increase in driving head pressure the gradient was increased to 58 for SG-3 and 57 for SG-4. Sample SG-3 was permeated with chemical for 0.32 day with an accumulated chemical flow of 9.3 pore volumes. Sample SG-4 was permeated with xylene for 0.77 day with a sum chemical flow of 8.0 pore volumes. Both samples exhibited similar behavior but yielded chemical leachate equilibrium permeabilities with a twofold difference. SG-3 had a permeability of 1.2 x 10^{-4} cm/sec as compared to 2.7 x 10^{-4} cm/sec for SG-4. Each of these values is about one order of magnitude larger than the corresponding baseline permeability on water.

The stair step nature of the curves is caused by the three intermittent percolation periods with seven day rest periods in between. The immediate breakdown of permeability for these glyoxal-modified sodium silicate samples does not parallel the decrease in permeability exhibited by the sodium aluminate-modified sodium silicate samples which were permeated at very similar gradients. In addition, SG-3 and SG-4 produced very small amounts of gas.

- Analysis of Permeability Test Results For Glyoxal-Modified Sodium Silicate Grout

The permeability of glyoxal-modified sodium silicate grout was tested

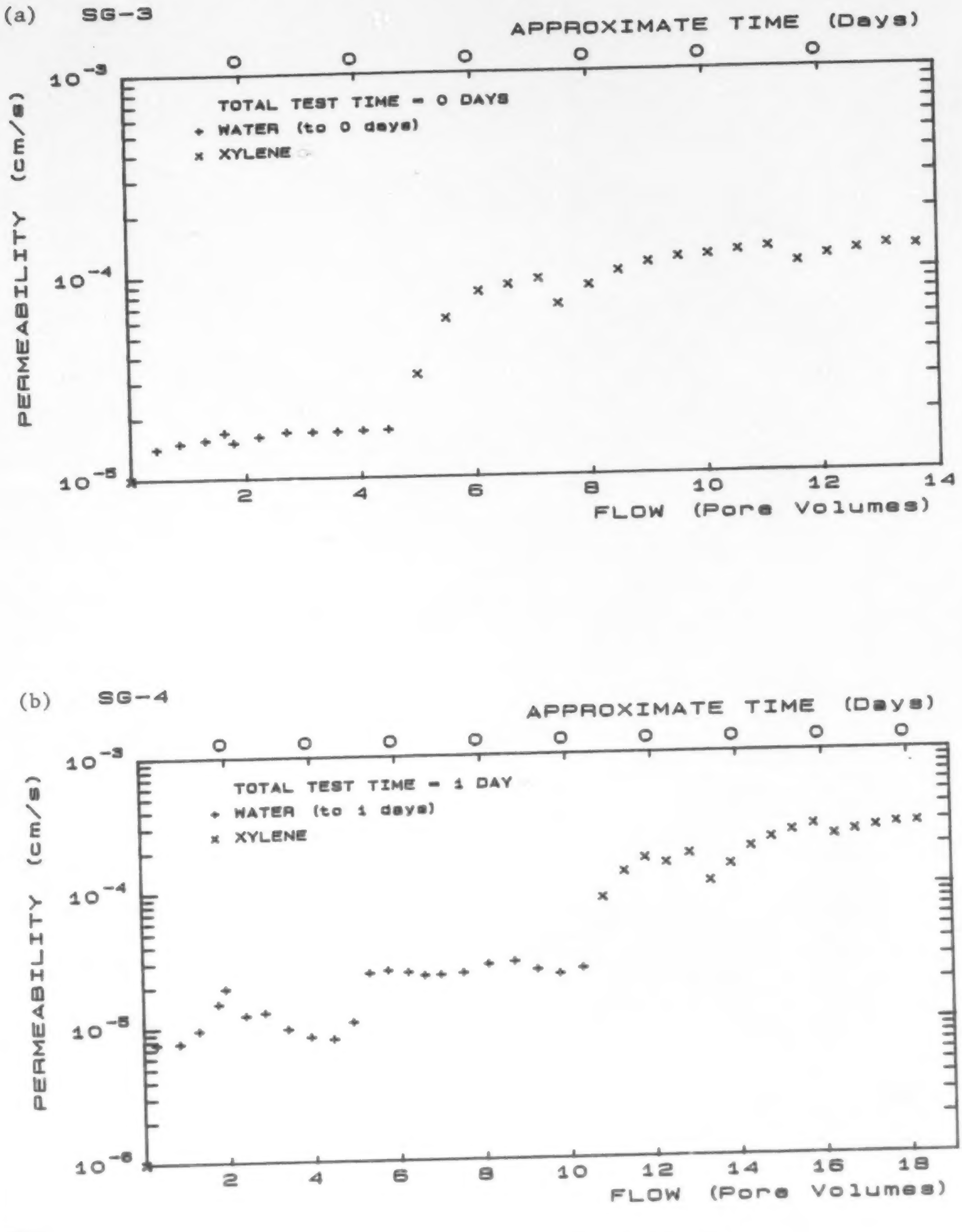


Figure 79. Permeability versus volume of flow of water and xylene through glyoxal-modified sodium silicate grout. (a) Plot for sample SG-3. (b) Plot for sample SG-4.

with water and three chemicals. The results from the tests with the chemicals were compared to that with the water in order to determine if the chemicals had any effect on the permeability of the grout. The results are summarized in the bar chart shown in Figure 80 (for an explanation of the notation, see the section titled Analysis of Permability Test Results for Acrylate Grout).

As shown in Figure 80, the permeability of this grout was quite uniform and relatively high with water, averaging 1.9 x 10^{-5} cm/sec. It was evident that the addition of glyoxal did not improve the permeability of the sodium silicate grout. Therefore the glyoxal-modified sodium silicate will probably not be used as a barrier around hazardous waste sites. However, to find general trends in its permeability, the grout was tested with three chemicals.

As shown in the bar chart in Figure 80, the chemicals had little effect on the permeability of the glyoxal-modified sodium silicate grout. Its permeability increased by about 0.75 order of magnitude with the permeation of reagent grade xylene. With the 20% solution of cupric sulfate the permeability of the grout decreased by approximately 0.6 order of magnitude, and the 25% solution of sodium hydroxide had a neglibible effect on this grout.

In summary, the glyoxal-modified sodium silicate grout had a relatively high permeability with deionized water. Two of the three chemicals tested had relatively little effect on its permeability, while the permeation of xylene caused an approximate 0.75 order of magnitude increase.

Permeability Tests of Sodium Aluminate-Modified Sodium Silicate Grout

During the discussion of the permeability of the sodium silicate grout, it was pointed out that its baseline permeability with water was too high for its use in barrier construction. In the preceding section the permeability of a glyoxal-modified sodium silicate was discussed, and that also had too high a baseline permeability. In this section the permeability test results of yet another version of sodium silicate grout, the sodium aluminate-modified sodium silicate grout, are presented. It was hoped that the addition of sodium aluminate would reduce the permeability of the hardened sodium silicate.

The sodium aluminate-modified sodium silicate grout mixed easily and was readily injected into a fine brown sandy soil. The samples made were 75 mm in diameter and varied between 64 to 71 mm in thickness. The cured samples were very hard and brown in color.

All the test samples were permeated with water prior to their testing with chemicals. This was done to saturate them and to obtain their equilibrium permeability with water. In addition, samples SA-3 and SA-4 were tested with water only, and to a pore volume flow of more than 34. The average final equilibrium permeability of all 8 grout samples was 1.7 x 10^{-5} cm/sec. This is considered to be a high permeability, and this grout too was a disappointment.

The following sections present the results of the permeability tests of sodium aluminate-modified sodium silicate grout samples with deionized water,

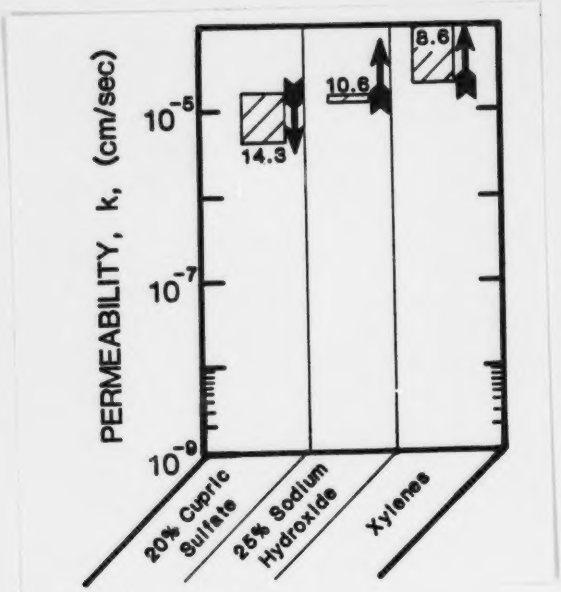


Figure 80. Permeability of glyoxal-modified sodium silicate grout with various chemicals.

20% solution of cupric sulfate, 25% solution of sodium hydroxide, and reagent grade xylene.

- Permeability Test of Sodium Aluminate-Modified Sodium Silicate Grout With Deionized Water

All sodium aluminate-modified sodium silicate grout samples were permeated with water before they were tested with chemicals. Their permeation continued at least until they reached equilibrium flow. Two of the samples were tested with water only, and their tests continued to an accumulated flow of more than 34 pore volumes. The two samples, SA-3 and SA-4, were initially tested with water at gradients of near 90, which were later dropped to 21 and 23, respectively. The gradient was reduced after 6.6 pore volumes of flow for sample SA-3, and 3.5 pore volumes of flow for sample SA-4. As shown in Figure 81, the two samples, SA-3 and SA-4, seemed to have come to equilibrium after 3 and 3.5 pore volumes of flow, respectively, but when the gradients were changed, both samples underwent a jump in their permeabilities. After the jumps, they came to new equilibrium states. The average equilibrium permeability of the 8 samples after an average pore volume flow of 3.9 was 9.2×10^{-6} cm/sec, but due to the change in gradients and the jump in the permeability of the two water samples, the average final equilibrium of the 8 samples on water was 1.7×10^{-5} cm/sec. In either case, the permeability of the sodium aluminate-modified sodium silicate grout with water was found to be too high for its use in cutoff construction.

- Sodium Aluminate-Modified Sodium Silicate Grout Samples Permeated With 20% Cupric Sulfate Solution

Two sodium silicate grout samples modified with sodium aluminate, designated SA-6 and SA-7, were tested with a 20% solution of cupric sulfate in water. Each sample had a diameter of 75 mm. Sample SA-6 had a thickness of 71 mm and SA-7 a thickness of 67 mm. Figure 82 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SA-6 was permeated with water for 1.2 days with an accumulated flow of 8.3 pore volumes. Sample SA-7 was tested on water for 1.2 days with an accumulated flow of 8.3 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero. The gradients varied somewhat due to the difference in sample thicknesses. Sample SA-6 had a gradient of 20 and SA-7 a gradient of 21. The water permeability versus pore volume flow curves show little variation. The curve for SA-6 indicates an equilibrium permeability of 7.9×10^{-6} cm/sec compared to 7.2×10^{-6} cm/sec for SA-7.

A 20% cupric sulfate solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi) and the back pressure at zero. However, due to an increase in driving headpressure the gradient was increased to 50 for SA-6 and 52.5 for SA-7. Sample SA-6 was permeated with chemical for 2.7 days with an accumulated chemical flow of 14.5 pore volumes. Sample SA-7 was permeated with a 20% solution of cupric sulfate for 2.7 days with a sum chem-

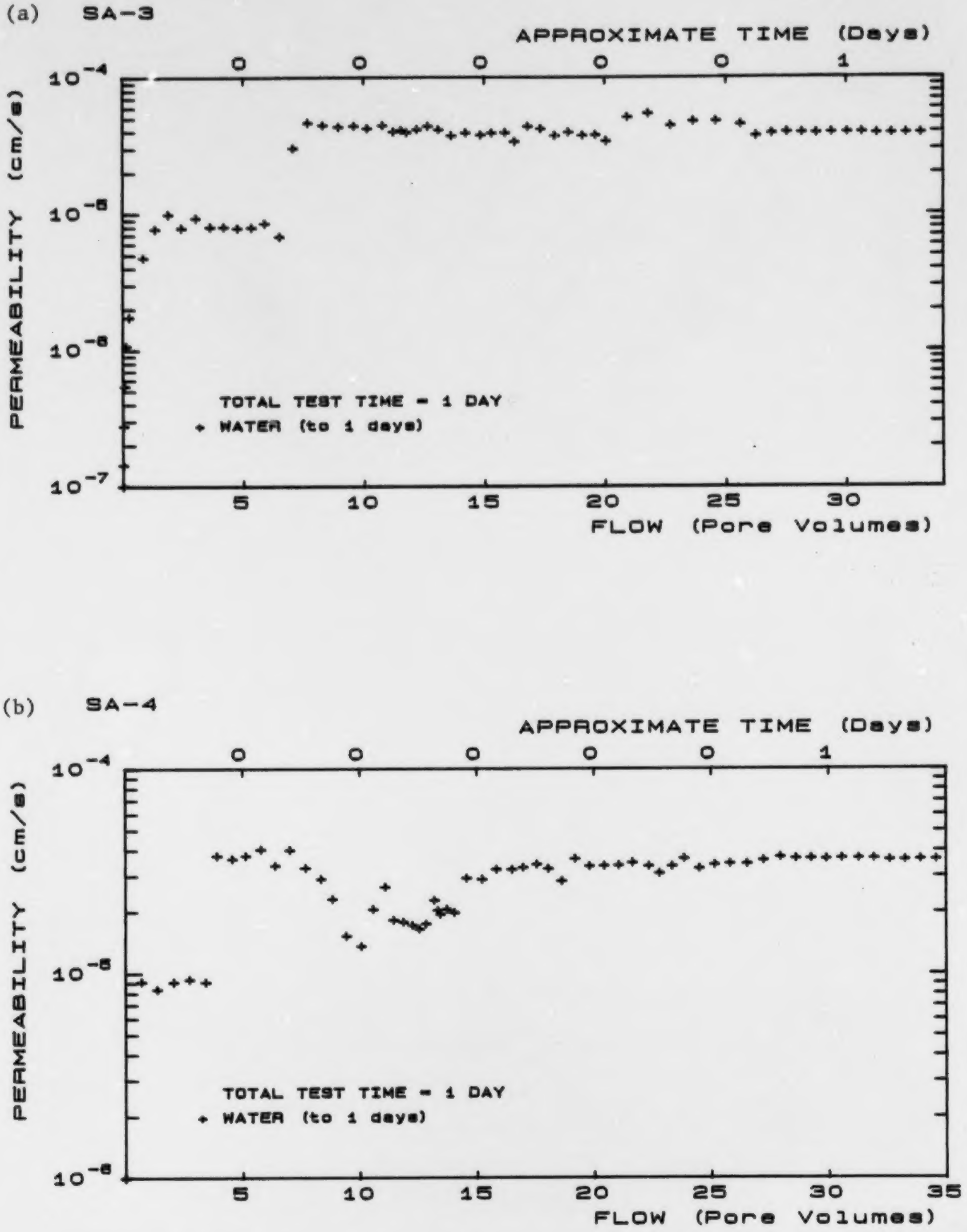
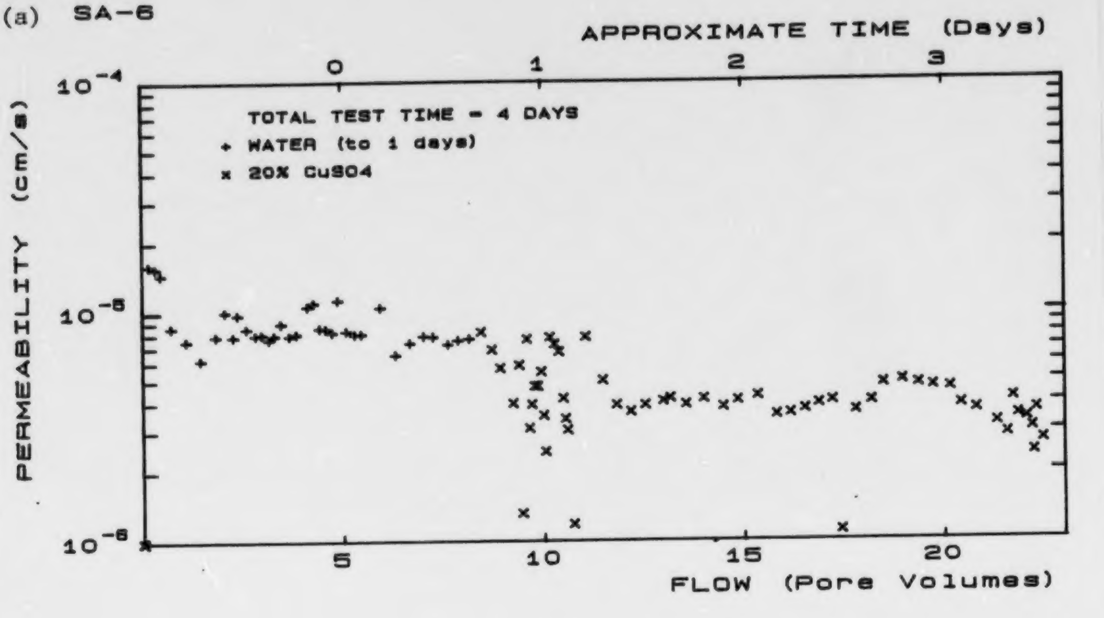


Figure 81. Permeability versus volume of flow of water through sodium aluminate-modified sodium silicate grout. (a) Plot for sample SA-3. (b) Plot for sample SA-4.



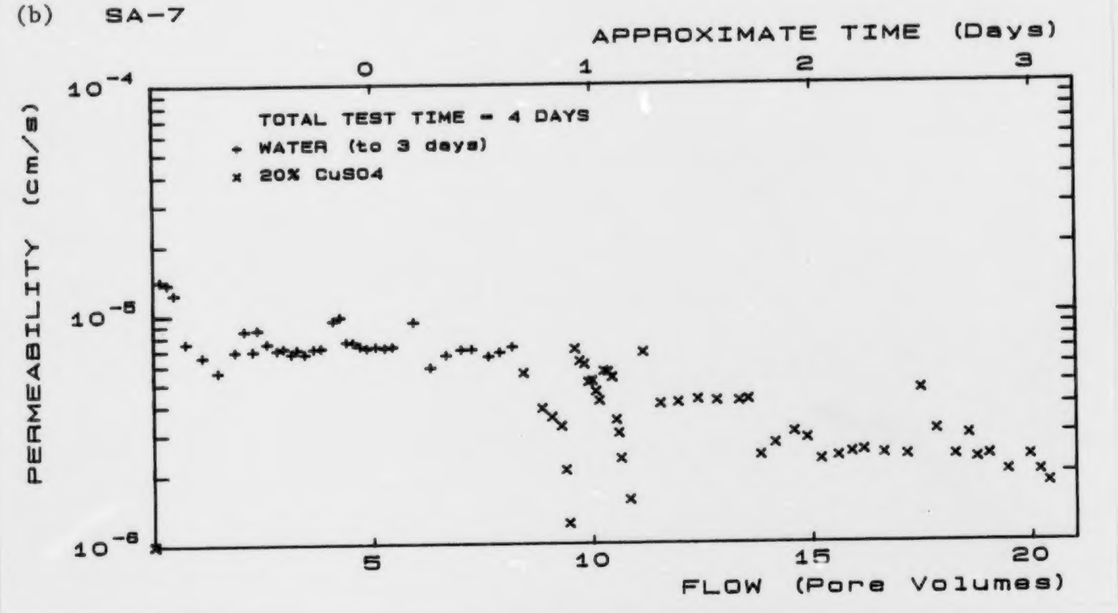


Figure 82. Permeability versus volume of flow of water and 20% cupric sulfate through sodium aluminate-modified sodium silicate grout. (a) Plot for sample SA-6. (b) Plot for sample SA-7.

ical flow of 12.4 pore volumes. Identical behavior was exhibited by each of the samples when chemical leachate was introduced.

The samples were initially permeated on chemical with a gradient of 20 and 21 for SA-6 and SA-7, respectively. This translated into a driving head pressure of 13.8 kPa (2.0 psi) and a backpressure of zero. The driving head pressure eventually had to be increased to 34.5 kPa (5.0 psi) (a gradient of 50 for SA-6 and 52.5 for SA-7) to overcome the pressure buildup caused by the large volume of gas production of the chemical leachate/grouted soil reaction. Approximately 2.6 pore volumes were percolated before this increase, at which time the effluent acquired a bluish tint which is the normal color of cupric sulfate. The final equilibrium permeability (in spite of the scatter of the plotted points) was determined to be 3.1 x 10^{-6} cm/sec for SA-6 and a very similar value of 2.1 x 10^{-6} cm/sec for SA-7. These are both slight decreases in permeability relative to their water baseline permeabilities.

- Sodium Aluminate-Modified Sodium Silicate Grout Samples Permeated With a 25% Sodium Hydroxide Solution

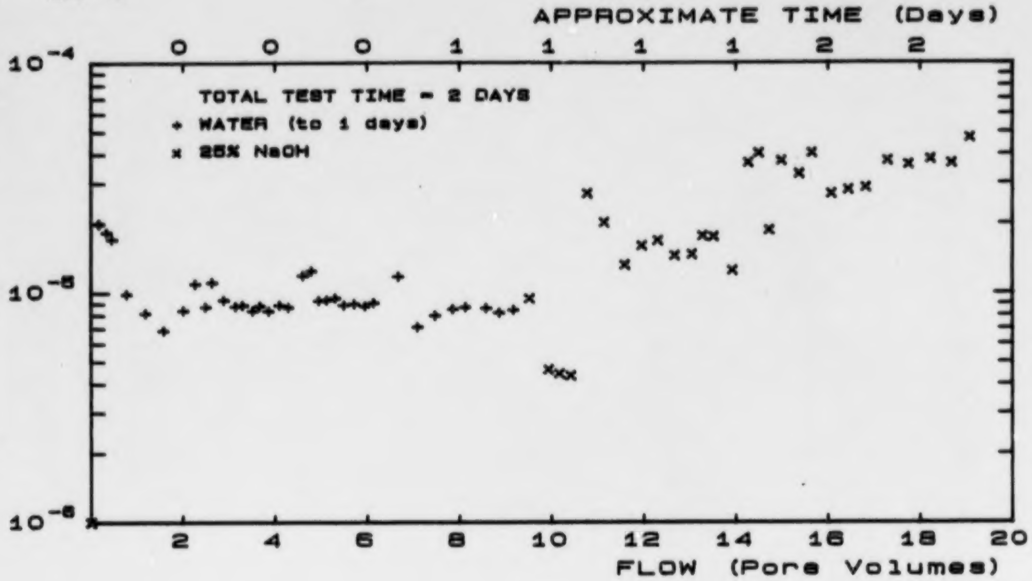
Two sodium aluminate-modified sodium silicate grout samples, designated SA-8 and SA-9, were tested with a 25% solution of sodium hydroxide in water. Each sample had a diameter of 75 mm. Sample SA-8 had a thickness of 67 mm and SA-9 a thickness of 71 mm. Figure 83 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SA-8 was permeated with water for 1.2 days with an accumulated flow of 9.3 pore volumes. Sample SA-9 was tested on water for 1.2 days with an accumulated flow of 7.3 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero. The gradients varied somewhat due to the difference in sample thicknesses. Sample SA-8 had a gradient of 21 and SA-9 a gradient of 20. The water permeability versus pore volume flow curves show little variation. The curve for SA-8 indicates an equilibrium permeability of 8.8 x 10^{-6} cm/sec as compared to 7.0 x 10^{-6} cm/sec for SA-9.

A 25% sodium hydroxide solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi), the backpressure at zero, and the gradients at 21 for SA-8 and 20 for SA-9. Sample SA-8 was permeated with chemical for 0.96 day with an accumulated chemical flow of 10.0 pore volumes. Sample SA-9 was permeated with the chemical for 0.98 day with a sum chemical flow of 8.7 pore volumes. Both samples behaved in a similar fashion when subjected to chemical leachate.

The permeabilities initially decreased until approximately one and two pore volumes of leachate percolated through samples SA-8 and SA-9, respectively, at which time the permeabilities increased abruptly. In addition, the effluent had precipitated brownish particles in it. Approximately one and a half pore volumes passed before the effluent exhibited no particles in suspension. Shortly thereafter the effluent also became clear. The permeabilities gradually increased until reaching an equilibrium of 4.0 x 10^{-5} cm/sec for SA-8 and 4.5 x 10^{-5} cm/sec for SA-9.

(a) SA-8



(b) SA-9

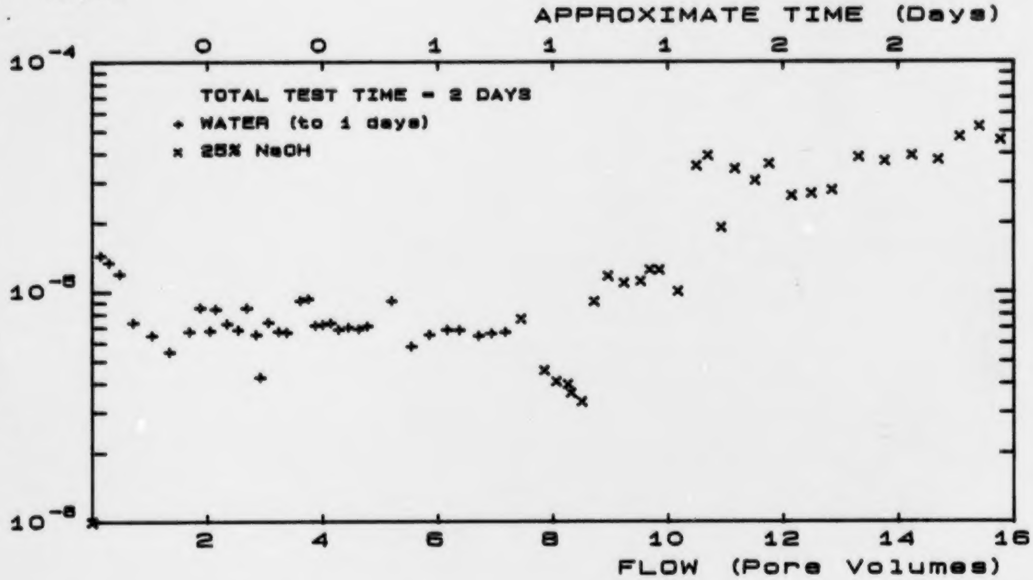


Figure 83. Permeability versus volume of flow of water and 25% sodium hydroxide through sodium aluminate-modified sodium silicate grout. (a) Plot for sample SA-8. (b) Plot for sample SA-9.

Due to the magnitudes of the permeabilities, the testing process had to be manned constantly. Therefore, intermittent percolation periods had to be performed with varying rest periods, generally one to seven days, in between. Both samples were permeated with chemical leachate over a period of 17 days. A total of six percolation periods were performed within this time.

- Sodium Aluminate-Modified Sodium Silicate Grout Samples Permeated With Reagent Grade Xylene

Two sodium silicate grout samples modified with sodium aluminate, designated SA-2 and SA-5, were tested with xylene. Each sample had a diameter of 75 mm. Sample SA-2 had a thickness of 64 mm and SA-5 a thickness of 70 mm. Figure 84 shows the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample SA-2 was permeated with water for 19.8 days with an accumulated flow of 9.9 pore volumes. Sample SA-5 was tested on water for 0.74 day with an accumulated flow of 8.2 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero. The gradients varied somewhat due to the difference in sample thicknesses. Sample SA-2 had a gradient of 22 and SA-5 a gradient of 20. The water permeability versus pore volume flow curves show little variation after the passage of two pore volumes of deionized water. The curve for SA-2 indicates an equilibrium permeability of 1.2 x 10^{-5} cm/sec as compared to 1.3 x 10^{-5} cm/sec for SA-5. During the permeation process the effluent acquired a dark brownish tint but eventually cleared.

Reagent grade xylene was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi). The backpressure was maintained at zero. Due to an increase in driving headpressure, the gradient was increased to 55 for SA-2 and to 50 for SA-5. Sample SA-2 was permeated with chemical for 39.0 days with an accumulated chemical flow of 8.4 pore volumes. Sample SA-5 was permeated with xylene for 29.2 days with a sum chemical flow of 6.6 pore volumes. The samples behaved in a similar manner. After the introduction of chemical the permeability decreased substantially. The permeability of sample SA-2 oscillated between 2.4 x 10^{-8} cm/sec and 2.7 x 10^{-9} cm/sec, while that of SA-5 ranged in values from 9.8 x 10^{-8} cm/sec to 3.4 x 10^{-10} cm/sec with an average equilibrium permeability of 3.2 x 10^{-9} cm/sec. This is approximately threefold smaller than that of SA-2.

Gradients were then increased to 275 and 252 for SA-2 and SA-5, respectively. At the same time the net confining pressure and backpressure were unchanged from original levels of 120.8 kPa (17.5 psi) and zero, in stated order. The final equilibrium permeabilities reached similar plateaus of 9.7 x 10^{-6} cm/sec for SA-2 as compared to 1.3 x 10^{-5} cm/sec for SA-5. In conclusion, variances in gradient seem to have a profound effect on the permeability of sodium silicate samples modified with sodium aluminate when permeated with xylene. This behavior was not exhibited in the glyoxal-modified sodium silicate samples that were permeated with xylene.

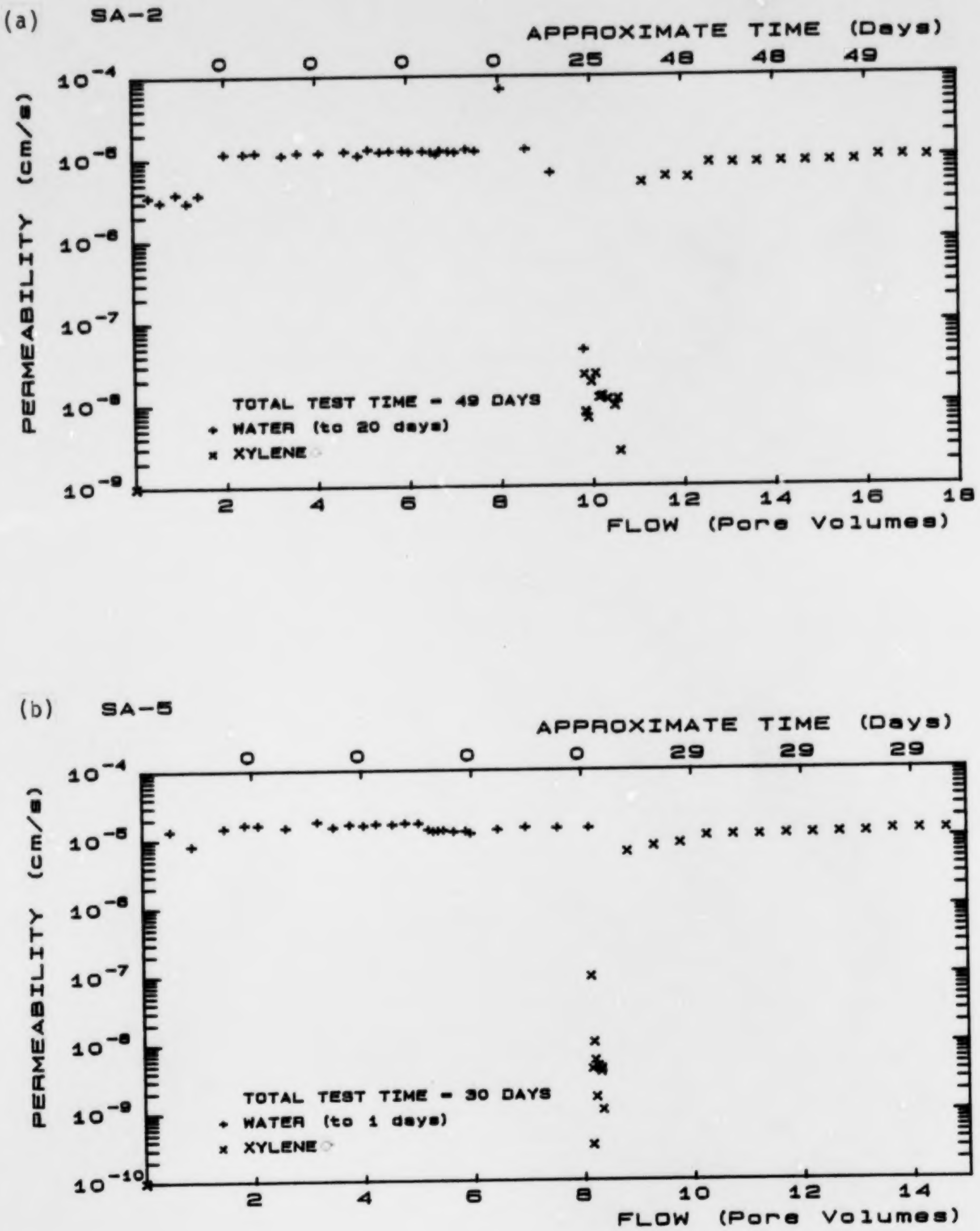


Figure 84. Permeability versus volume of water and xylene through sodium aluminate-modified sodium silicate grout. (a) Plot for sample SA-2. (b) Plot for sample SA-5.

- Analysis of Permeability Test Results For Sodium Aluminate-Modified Sodium Silicate Grout

The sodium aluminate-modified sodium silicate grout was tested with deionized water and three chemicals in order to determine how the permeability of this grout with water compared with those obtained as final permeabilities with the chemicals. The summary of the results is shown on the bar chart in Figure 85. (For an explanation of the notation in the bar chart, see the section titled Analysis of Permeability Test Results for Acrylate Grout.)

As shown in Figure 85, the sodium aluminate-modified sodium silicate grout was found to be quite pervious with deionized water. Its baseline permeability with water varied somewhat, but averaged approximately 1.9 x 10^{-5} cm/sec, a relatively high value. The sodium aluminate modifier was added to the sodium silicate grout to decrease its permeability, however, the desired results were not achieved.

Even though this grout will probably not be considered for use in cutoff construction because of its high permeability, it was tested with three chemicals in order to obtain information on its general behavior with chemicals. The chemical permeants used were: 20% solution of cupric sulfate, 25% solution of sodium hydroxide, and reagent grade xylene. The 20% solution of cupric sulfate caused a slight reduction in the permeability of the grout. The reagent grade xylene induced a more than 3 orders of magnitude temporary decrease in the permeability with 0.5 pore volume of flow, but after that the permeability started to increase and finally terminated at near baseline permeability with water. The only chemical of the three to cause an increase in the permeability of the grout was the 25% solution of sodium hydroxide producing an increase of approximately 0.6 order of magnitude.

In summary, the sodium aluminate-modified sodium silicate grout had relatively high baseline permeabilities with deionized water. The three chemicals used had relatively little to no effect on the permeability of the sodium aluminate-modified sodium silicate grout samples.

Permeability Tests of Urethane Grout

The urethane grout was selected as one of the first two grouts to be tested in this study. The other was the acrylate grout. This grout has a low viscosity for easy grouting, it is non-toxic, it is easy to mix and handle, has a relatively long set time, and once it has set, it hardens quickly. The grout had an average permeability of 3.6 x 10^{-9} cm/sec with water, which is considered low and makes this grout a good candidate for use in barrier construction. The urethane grout also has good mechanical strength to resist erosion due to moving water.

For this project, the urethane grout samples were made by injecting the grout into a medium silica sand. The mixing of the grout, its handling, and the injection process were relatively easy. The resulting samples were very uniform with respect to appearance and permeability. They had the consistency of medium hard rubber, and their color was off-white. The samples were made to be 75 mm in diameter and approximately 34 mm thick. They were made thin

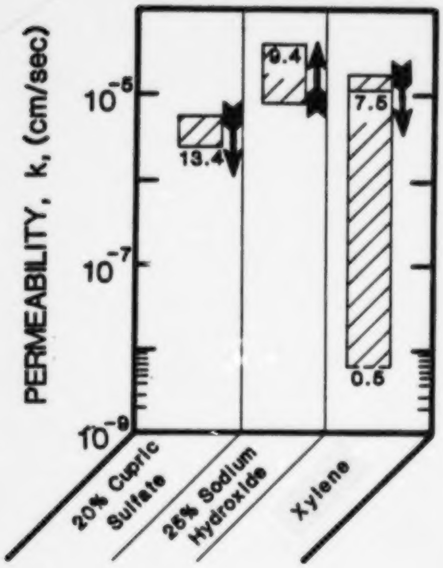


Figure 85. Permeability of sodium aluminate-modified sodium silicate grout with various chemicals.

to reduce the testing time. For the same reason, high gradients were used in the permeability tests. The effect of these gradients on the samples were checked, and were found to be small (see the results in the following section.)

In this research program the permeability of urethane grout was tested with the following permeants: deionized water, 100% solution of acetone, reagent grade aniline, 20% solution of cupric sulfate, 100% and 25% solutions of ethylene glycol, 4N and 1N solutions of hydrochloric acid, 100% solution of methanol, real-site paint waste, real-site refinery waste, 25% and 10% solutions of sodium hydroxide, and reagent grade xylene.

In order to have a check on the results, two or more urethane samples were tested with every permeant.

- Permeability Test of Urethane Grout With Deionized Water

All urethane grout samples were first tested with water in order to saturate them prior to the introduction of chemicals. Practically all the samples were permeated with water until they achieved equilibrium or until at least one pore volume of flow had taken place. The average equilibrium or final permeability of the first 28 samples tested with water was found to be 3.6×10^{-9} cm/sec, a relatively low permeability. The median permeability of the 28 samples was 2.6×10^{-9} cm/sec. The average flow with water for these samples was 2.7 pore volumes.

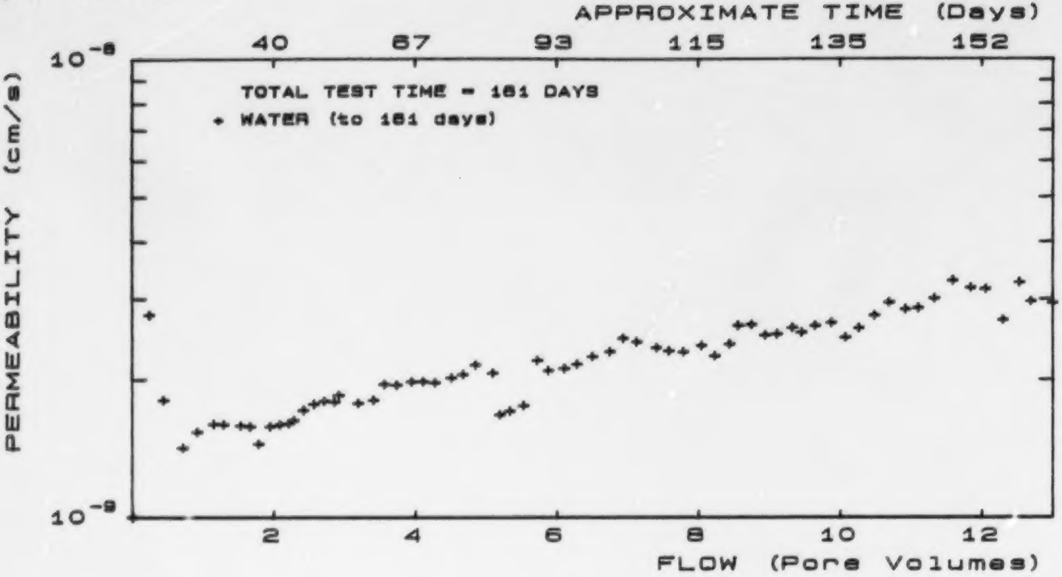
For a more detailed analysis, urethane samples UR-42 and UR-43 each were tested with water alone for over 12 pore volumes of flow and for more than 150 days (see Figure 86). Except for the first 0.45 pore volumes of flow, they were tested at a headpressure of 242 kPa (35 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). The starting gradient for sample UR-42 was 176, and 362 for sample UR-43. After approximately 0.45 pore volume of flow, both gradients were raised to 517. Following that, both samples quickly came to a stable behavior, exhibiting a very gradual and uniformly increasing permeability with water flow. At the vicinity of 1 pore volume of flow, sample UR-42 had a permeability of 1.4×10^{-9} cm/sec. With continued flow the permeabilities of the two samples increased at a constant rate, and over the next 11 pore volumes of flow reached 3.2×10^{-9} cm/sec and 3.3×10^{-9} cm/sec, respectively, a very moderate increase. It was concluded that the use of the high gradient did not cause excessive changes in the permeability of the urethane grout and its use in this testing program was permissible.

To summarize, the urethane grout behaved well with water, its average permeability of 3.6×10^{-9} cm/sec is a low value that makes this grout a prime candidate for its use in barrier construction.

- Permeability Test of Urethane Grout With 100% Acetone

Four urethane grout samples, UR-9, UR-25, UR-10, and UR-7, were tested with 100% acetone. Their thicknesses were 25, 35, 24, and 30 mm, respectively, and all four were 75 mm in diameter. Figures 87 and 88 show the permeability

(a) UR-42



(b) UR-43

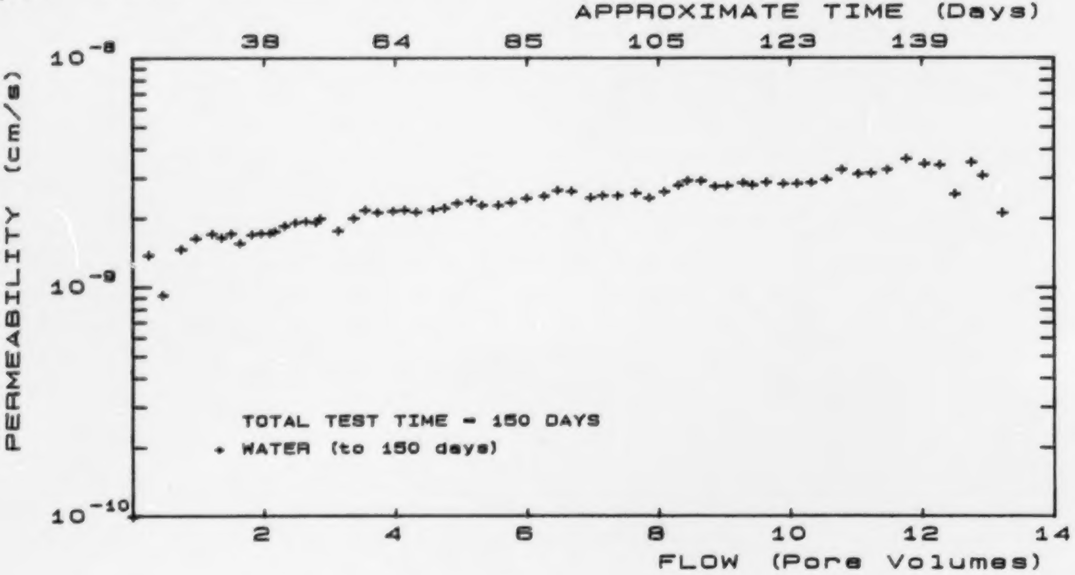
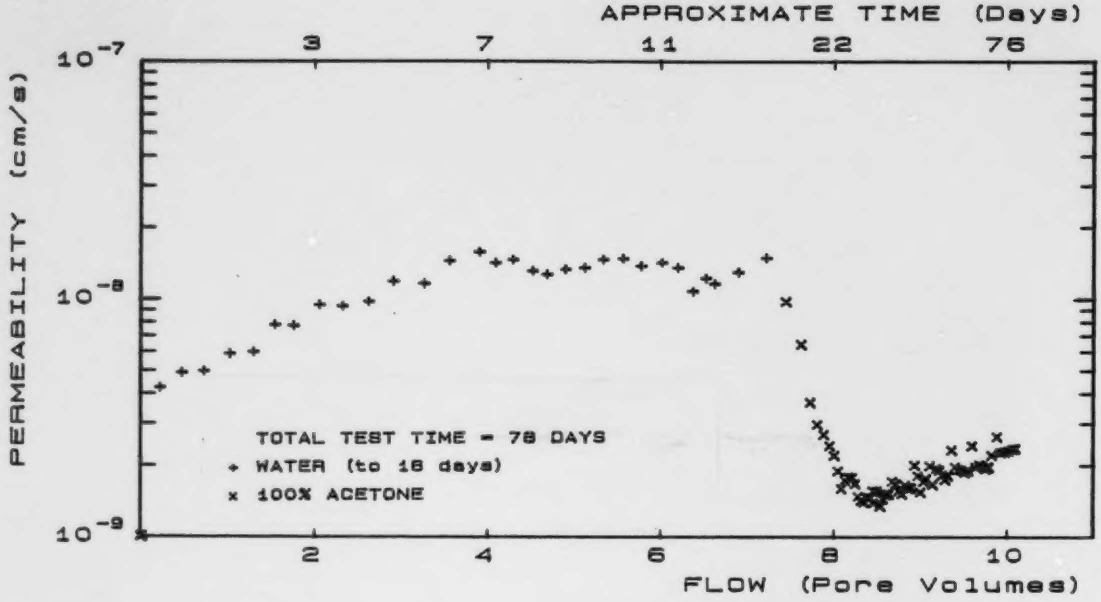


Figure 86. Permeability versus volume of flow of water through urethane grout. (a) Plot for sample UR-42. (b) Plot for sample UR-43.

(a) UR-9



(b) UR-25

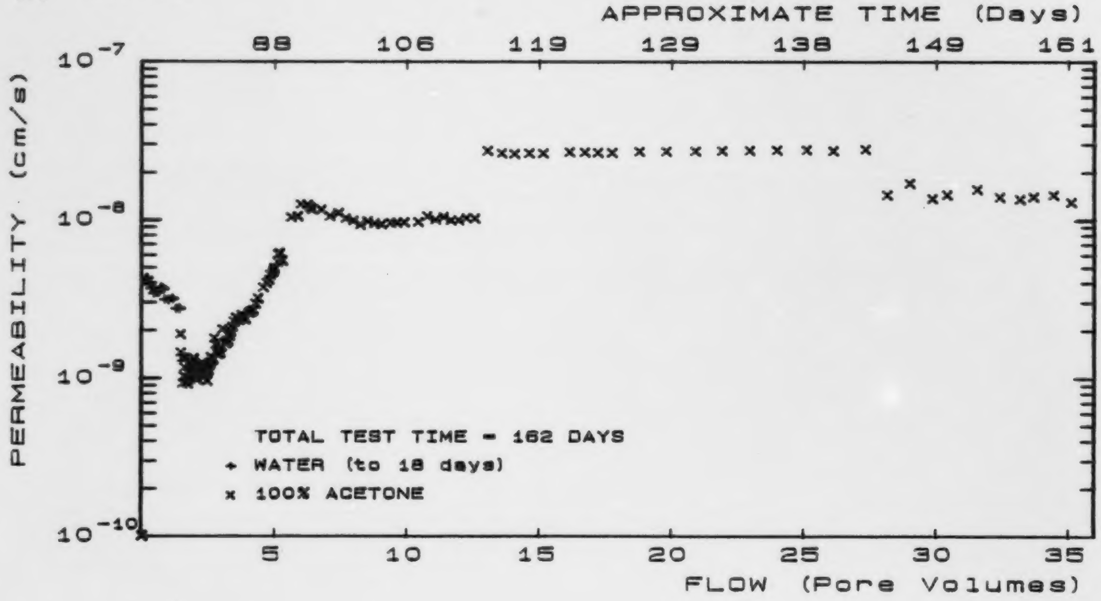
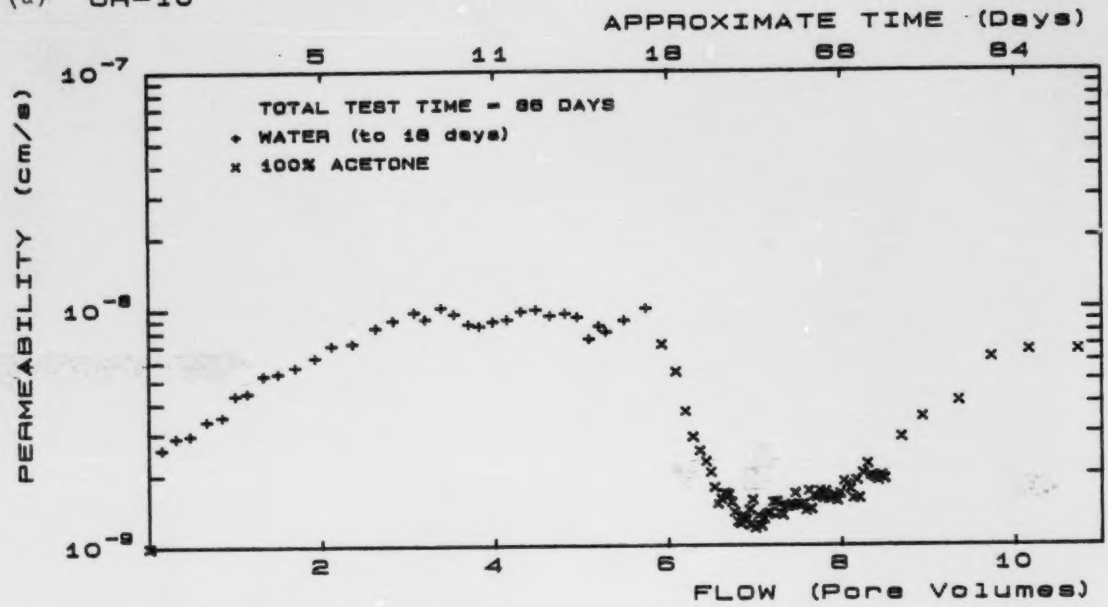


Figure 87. Permeability versus volume of flow of water and 100% acetone through urethane grout. (a) Plot for sample UR-9. (b) Plot for sample UR-25.

(a) UR-10



(b) UR-7

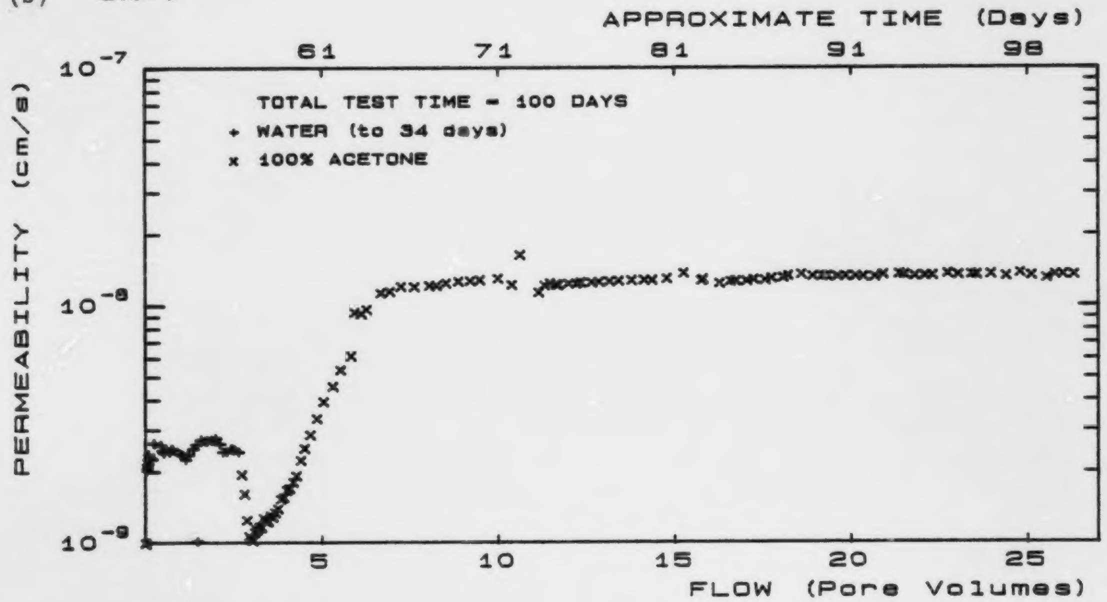


Figure 88. Permeability versus volume of flow of water and 100% acetone through urethane grout. (a) Plot for sample UR-10. (b) Plot for sample UR-7.

versus flow test plots for the four samples.

As can be seen in Figure 87, sample UR-9 was tested on water for an extended period of more than 6 pore volumes of flow and came to an equilibrium at a permeability of 1.4 x 10^{-8} cm/sec. Following the introduction of acetone, the permeability of the sample decreased by about one order of magnitude, to a permeability of 1.4 x 10^{-9} cm/sec. After that, the permeability of the sample began to rise. However, the testing of the sample was completed after two pore volumes of flow on acetone, which, as it turned out, was before the sample had an opportunity to reach equilibrium. Therefore, the test of sample UR-9 on acetone is considered incomplete.

Preceding the introduction of 100% acetone, sample UR-25 was saturated with water. The water permeation through the sample was accomplished at a headpressure of 172.5 kPa (25 psi), a backpressure of 69 kPa (10 psi), a net confining pressure of 120.8 kPa (17.5 psi), and a gradient of 302. The permeability versus flow curve for water showed fairly stable characteristics. Sample UR-25 came to an equilibrium at a permeability of 3.0 x 10^{-9} cm/sec after 1.4 pore volumes of flow and 19 days.

The acetone was introduced into sample UR-25 at the pressure conditions used with water, and at a gradient of 380. Upon the introduction of acetone, the permeability versus pore volume flow curve shown in Figure 87 took a sharp turn down. It bottomed out at 9.9 x 10^{-10} cm/sec after 0.7 pore volume of flow and 20 days on acetone. Thereafter the permeability of the sample began a gradual rise and, after 74 days and 4.6 total pore volumes of flow on acetone, it peaked at a permeability of 1.3 x 10^{-8} cm/sec, dropped off slightly and then rose again to reach a final equilibrium permeability of 1 x 10^{-8} cm/sec after 10 pore volumes of flow on acetone. The whole test was conducted for 98 days and 11.7 total pore volumes on acetone. As shown, this sample came to a stable equilibrium permeability at the end of its test.

The saturation of sample UR-10 with water took place under varying pressure conditions and varied gradients. This sample was one of the early test samples, and the variation in pressures and gradients was due to experimentation with these variables. The very high initial gradient of 1026 may explain the initial rise in the permeability of this sample with water. This sample was permeated with water at a constant backpressure of 34.5 kPa (5 psi), however, both headpressure and net confining pressure varied. The headpressure started out at 276 kPa (40 psi) and was gradually decreased to 82.8 kPa (12 psi). The net confining pressure started out at 190 kPa (27.5 psi) and was also gradually reduced to 93 kPa (13.5 psi). Corresponding to the headpressure variations, the gradient varied from an initial 1026 to a final value of 205. After 3.4 pore volumes of flow on water the sample came to equilibrium at a permeability of 9 x 10^{-9} cm/sec. The sample was tested with water for a total of 5.8 pore volumes of flow.

Acetone was introduced into the sample at a headpressure of 82.8 kPa (12 psi), a backpressure of 34.5 kPa (5 psi), a net confining pressure of 93 kPa (13.5 psi), and a gradient of 259. For most of the test the headpressure was held at 76 or 69 kPa (11 and 10 psi), the backpressure at 34.5 kPa (5 psi), and the net confining pressure at 97 or 100 kPa (14 and 14.5 psi).

The gradient was held at 259 and 222, respectively. However, at the very end of the test the sample was put under a headpressure of 173 kPa (25 psi) while maintaining a backpressure of 34.5 kPa (5 psi). The net confining pressure was at 138 kPa (20 psi) and the gradient was at 739. With the introduction of acetone, the permeability of the sample quickly dropped by almost one order of magnitude to a low value of 1.2×10^{-9} cm/sec after 20 days and 1.3 pore volumes of flow on acetone. Following this period the permeability of the sample started to rise, first at a slow rate, then at a faster rate, and came to a final equilibrium at 6.8×10^{-9} cm/sec, after 5 pore volumes of flow and 68 days on acetone. As can be seen in Figure 88, the permeability readings on the sample were steady over one pore volume of flow, and the permeability versus flow curve of the sample is very similar to that of sample UR-25. Therefore, it is believed that the permeability versus flow curve for sample UR-10 gave valid information on the equilibrium permeability of urethane grout with acetone. However, for more reliable information, this sample should have been tested a little longer. This sample showed the least change in permeability with acetone flow among the replicates. The reason for this may be that the sample was the most thoroughly saturated of the three samples, as it stayed on water for 5.8 pore volumes of flow.

Preceding the introduction of acetone, sample UR-7 was saturated with water at a headpressure that varied between 69 kPa (10 psi) and 173 kPa (25 psi), a constant backpressure of 34.5 kPa (5 psi), and a net confining pressure that varied between 86 and 138 kPa (12.5 and 20 psi). The gradient varied from 117 to 469. As shown in Figure 88, after a small initial rise, the sample exhibited a fairly steady permeability of approximately 2.5×10^{-9} cm/sec after 2.8 pore volumes of water flow and 37 days of testing.

Acetone was introduced into sample UR-7 at a headpressure of 173 kPa (25 psi), a backpressure of 34.5 kPa (5 psi), and a net confining pressure of 138 kPa (20 psi). A gradient of 592 was used. With the introduction of acetone, the permeability of the sample rapidly decreased to 1.05×10^{-9} cm/sec with an acetone flow of 0.4 pore volume during a six-day period, then rose at a moderate rate to a final permeability of 1×10^{-8} cm/sec after 4.0 pore volumes of flow and 30 days of testing with acetone. The permeability versus pore volume flow curve of sample UR-7 resembles that of sample UR-25 up to four pore volumes of its flow with acetone. The permeability readings for sample UR-7 stayed fairly steady over 0.84 pore volume of flow and three days of testing with acetone; the permeability at this stage was identical to the final equilibrium permeability readings for sample UR-25. Again, in hindsight, it would have been better to test sample UR-7 a little longer. However, it is believed that the results shown in Figure 88 are valid and the sample did reach an equilibrium permeability at the termination of its testing.

In summary, the tests of the four urethane samples with acetone showed consistent results. The results indicated that the final equilibrium permeabilities with acetone were approximately 1×10^{-8} cm/sec and the rise in permeability from that with water to that with acetone at equilibrium was in the range of 0.7 to 0.75 order of magnitude (see samples UR-25 and UR-7).

- Permeability Test of Urethane Grout With Aniline

Two urethane grout samples, designated UR-20 and UR-21, were tested with aniline. Their diameter was 75 mm, and their thicknesses were 38 and 35 mm, respectively. Figure 89 shows the permeability test plots for these two samples.

The two urethane samples were saturated with water prior to the introduction of aniline. The water percolated through the samples at a net confining pressure of 121 kPa (17.5 psi), a headpressure of 173 kPa (25 psi), and a backpressure of 69 kPa (10 psi). Sample UR-20 was tested with water at a gradient of 281 over a period of 16 days and with a pore volume flow of 0.86. Sample UR-21 was tested for 19 days with an accumulated flow of 0.80 pore volume and a gradient of 302. For sample UR-20 the final permeability value with water was 3.0 x 10^{-9} cm/sec, while for sample UR-21 it was 2.1 x 10^{-9} cm/sec.

Aniline was introduced into the samples at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). The gradients for the two samples were held at 276 and 295, respectively, After the introduction of aniline, the permeability of both samples rose slightly, followed by a sharp drop in permeability, which later tapered off into a more gently falling permeability versus pore volume flow curve. The permeability of sample UR-20 continued to decrease to a minimum of 3.2 x 10^{-10} cm/sec at a cumulative pore volume flow of 1.08 on aniline. At that point, the curve started to rise gently and continued to rise until the end of the test, at which point it reached a permeability value of 5.6 x 10^{-10} cm/sec. This occurred after a total pore volume flow of 2.1 with aniline. Sample UR-21 behaved similarly to sample UR-20, in that its permeability continued to decrease gently until it bottomed out at a low value of 2.4 x 10^{-10} cm/sec after 1.21 pore volumes of flow with aniline. At that point, again very gently, the sample permeability started to rise, and at the end of the test reached a value of 2.8 x 10^{-10} cm/sec; this occurred at a total pore volume flow of 1.36 with aniline. It should be noted that sample UR-20 had a total test time of 235 days, of which 219 were with aniline. Sample UR-21 was tested over a period of 133 days, of which 114 were with aniline. It should also be noted that in both cases, at the termination of the tests, the permeabilities of the samples were at such a low level that they were practically impervious.

When the two permeability versus pore volume flow curves are compared, it is clear that both samples behaved essentially the same way. In both cases the aniline caused a reduction in permeability, and the low point in both curves occurred at about the same level. One may speculate that, given more testing time, the curves may have reversed and indicated a rise in permeability. There is a slight indication of that possibility in the results of sample UR-20, however, it is speculated that this change could have occurred only over a very long period of time.

An interesting experiment was performed with sample UR-20 after its regular test was terminated. The sample was left untouched for three months, after which it was put back on the testing line. It subsequently registered a

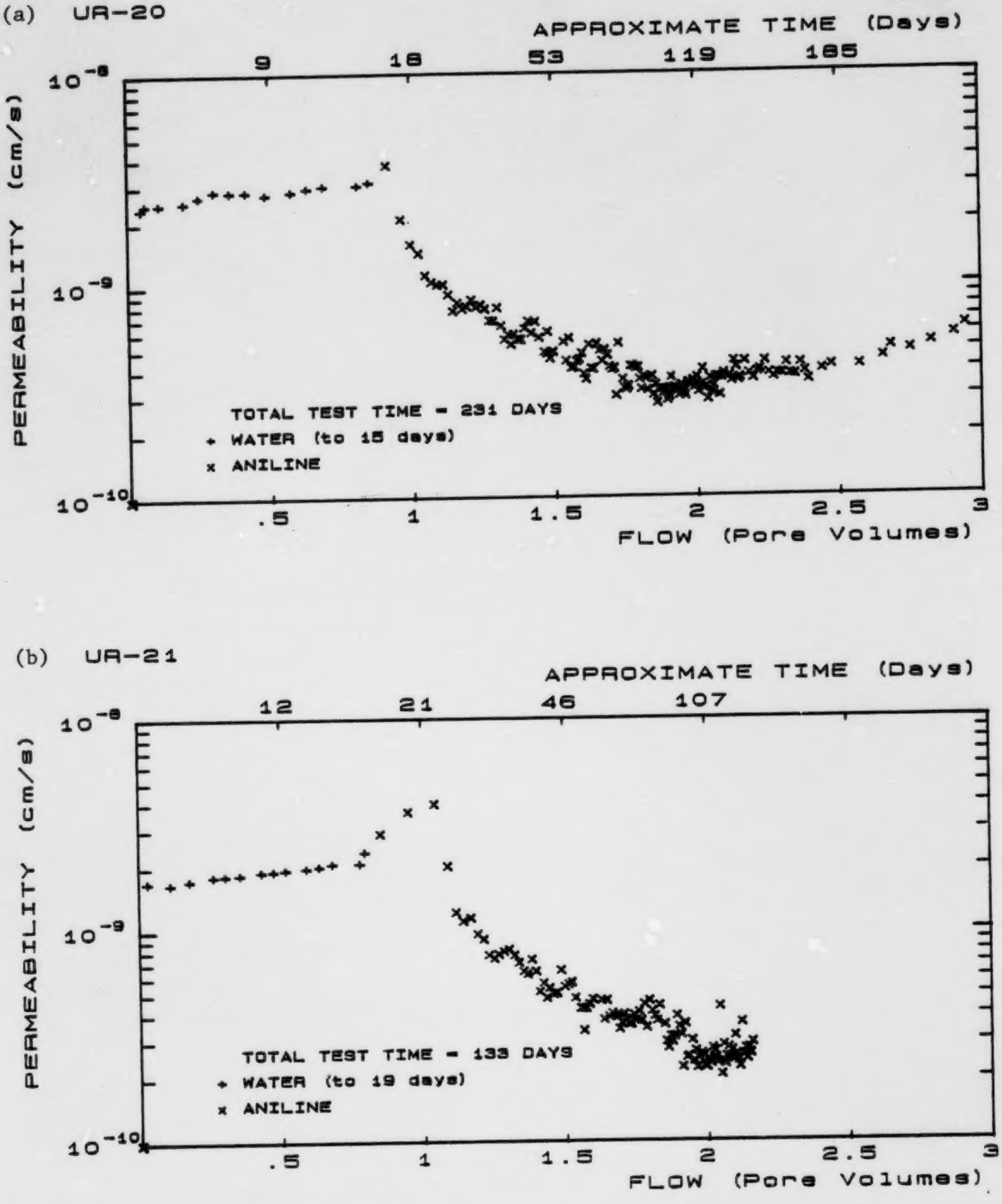


Figure 89. Permeability versus volume of flow of water and aniline through urethane grout. (a) Plot for sample UR-20. (b) Plot for sample UR-21.

permeability value of 8 x 10^{-7} cm/sec. This would represent a more than 3 orders of magnitude jump in permeability. It is most likely that this great increase in permeability was caused by the disintegration of the urethane grout with longtime exposure to aniline.

- Permeability Test of Urethane Grout With 20% Cupric Sulfate

Two urethane grout samples, UR-26 and UR-29, were tested with 20% cupric sulfate. Their thicknesses were 32 and 33 mm, respectively, and both were 75 mm in diameter. Figure 90 shows the permeability versus flow plots for the two samples. The testing of the samples started with water. The permeability tests were conducted at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi) for both samples. Samples UR-26 and UR-29 were tested with gradients of 330 and 325, respectively. Sample UR-26 was tested with water for a duration of 50 days and to a total pore volume flow of 2.91. Its equilibrium permeability was approximately 2.5 x 10^{-9} cm/sec. Sample UR-29 was tested with water for 23 days and to an accumulated pore volume flow of 1.8. Its equilibrium permeability was 3.0 x 10^{-9} cm/sec.

The introduction of cupric sulfate into the samples caused immediate increases in the permeabilities. For sample UR-26, the permeability versus flow curve rose to a peak permeability of 1.45 x 10^{-7} cm/sec after just one and one-half days of testing and with a flow of 1.12 pore volumes of cupric sulfate. The sample then experienced a decrease in its permeability which equilibrated at approximately 1 x 10^{-7} cm/sec after a flow of 2.3 pore volumes of cupric sulfate. The sample was tested for a total of 4.75 pore volumes of flow with cupric sulfate.

The permeability versus pore volume flow curve for sample UR-29 exhibited an initial sharp rise with cupric sulfate, which later tapered off to a more gentle rise. The permeability reached an upper level of 3.1 x 10^{-7} cm/sec in only one and one-half days of testing. The total accumulated flow with cupric sulfate at that time was 2.8 pore volumes. The permeability versus flow curve remained stable and showed an equilibrium permeability of 3.1 x 10^{-7} cm/sec from there on. The cupric sulfate flow was maintained for a total of 5.9 pore volumes.

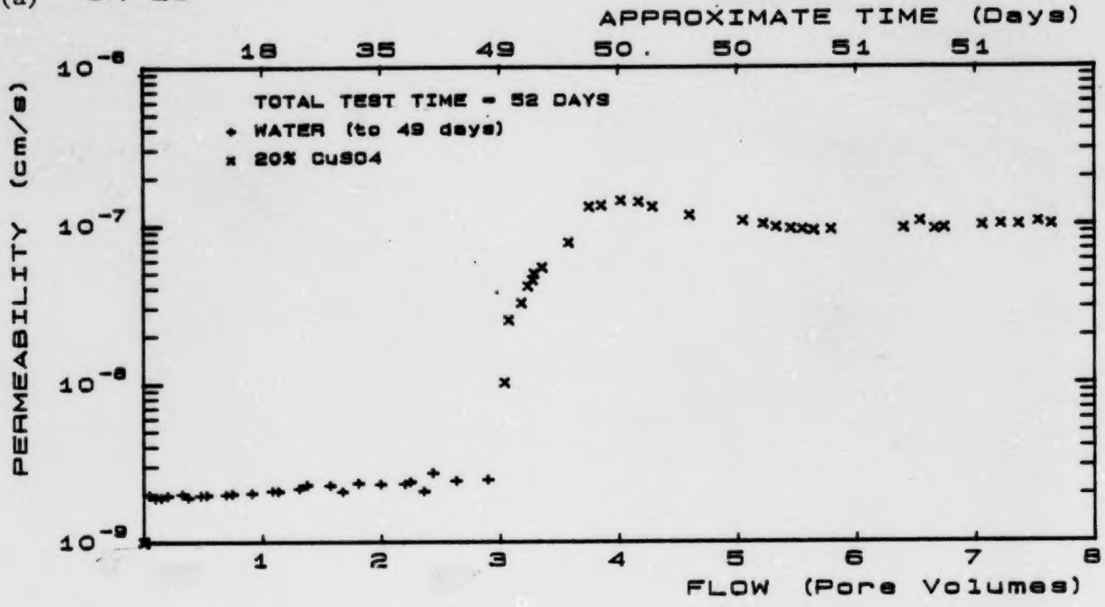
Both urethane samples on cupric sulfate were tested at pressure conditions identical to those used with water. The tests on the chemical were conducted at gradients of 289 and 285, on samples UR-26 and UR-29, respectively.

In comparing the permeability versus flow curves for the two samples, one may conclude that they behaved quite consistently; they had stable permeabilities with water and showed similar increases with the introduction of cupric sulfate. Both curves leveled off and the samples came to equilibrium. Their final equilibrium permeabilities were in good agreement.

- Permeability Test of Urethane Grout With 100% Ethylene Glycol

Figure 91 shows the permeability versus flow curves for two urethane

(a) UR-26



(b) UR-29

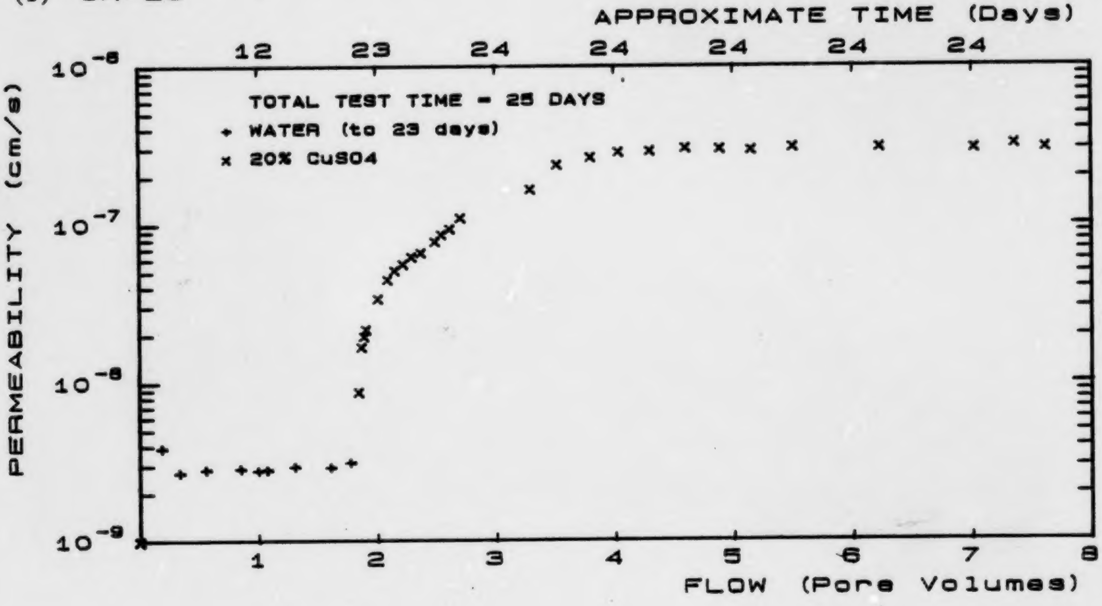
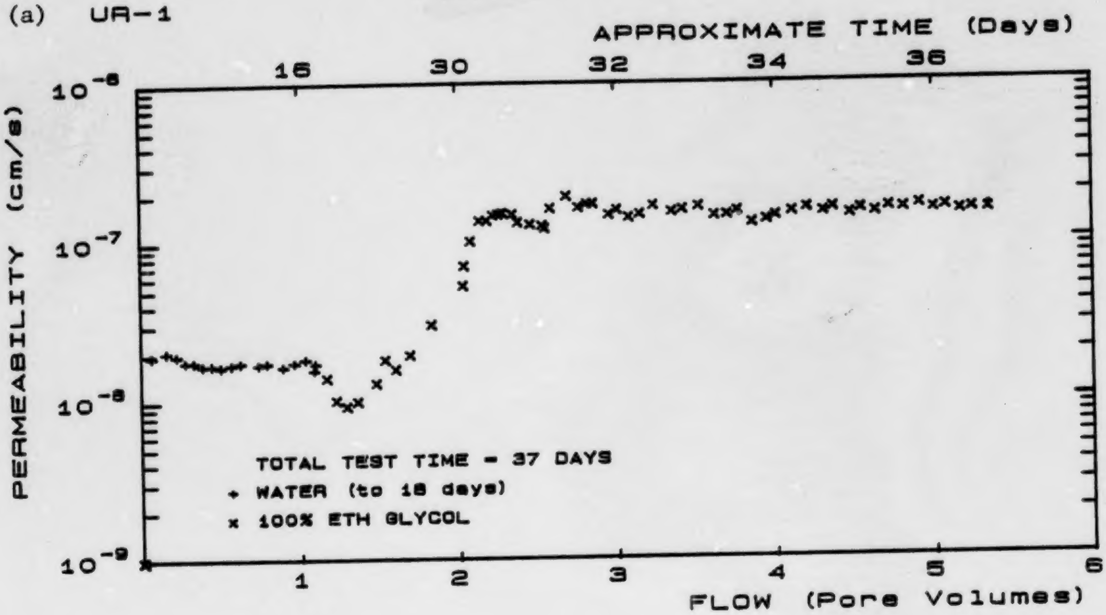


Figure 90. Permeability versus volume of flow of water and 20% cupric sulfate through urethane grout. (a) Plot for sample UR-26. (b) Plot for sample UR-29.

(a) UR-1



(b) UR-14

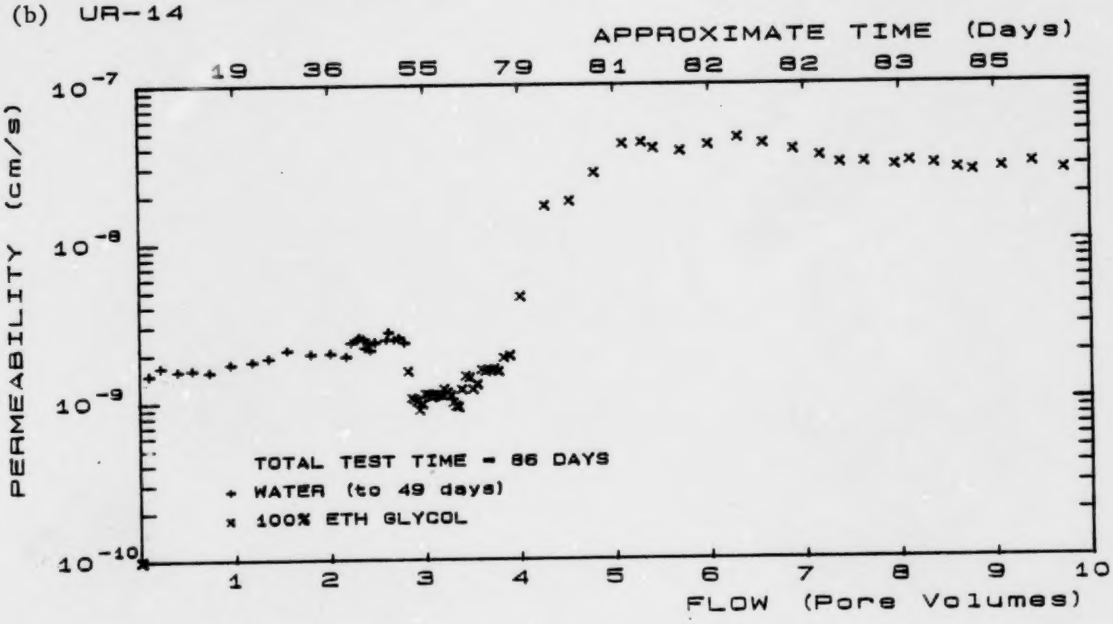


Figure 91. Permeability versus volume of flow of water and ethylene glycol through urethane grout. (a) Plot for sample UR-1. (b) Plot for sample UR-14.

samples with 100% ethylene glycol. The samples were designated as UR-1 and UR-14. Their thicknesses were 33 and 30 mm, respectively, and both were 75 mm in diameter.

Both samples were first tested on water in order to saturate them. Sample UR-1 was tested with water for 20 days, and sample UR-14 for 50 days. Sample UR-1 was permeated with water at a headpressure of 104 kPa (15 psi), a tailpressure of 34.5 kPa (5 psi), a net confining pressure of 173 kPa (25 psi), and at a gradient of 213. Sample UR-14 was started with water at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kpa (10 psi), a net confining pressure of 121 kPa (17.5 psi), and a gradient of 352. After a pore volume flow of 2.2 of water, the headpressure was dropped to 104 kPa (15.5 psi), the tailpressure to 21 kPa (3 psi), the net confining pressure to 110 kPa (16 psi), and the gradient to 281. These pressures were used until the end of the test with water. The nature of the permeability versus flow curves for both samples with water was fairly stable. The permeability of sample UR-1 decreased slightly from its initial value to an equilibrium value of 7.7 x 10^{-9} cm/sec after 2.6 pore volumes of flow. On the other hand, sample UR-14 exhibited a gently increasing permeability with water flow that came to an equilibrium at 2.6 x 10^{-9} cm/sec after 2.8 pore volumes of flow.

Ethylene glycol was introduced into sample UR-1 at a headpressure of 104 kPa (15 psi), a tailpressure of 0, a net confining pressure of 121 kPa (17.5 psi), and at a gradient of 287. After a flow of 3.5 pore volumes with ethylene glycol, the tailpressure was increased to 21 kPa (3 psi), and the net confining pressure was reduced to 110 kPa (16 psi), and the gradient to 230. In the case of sample UR-14, ethylene glycol was introduced at a headpressure of 104 kPa (16 psi), a tailpressure of 0, a net confining pressure of 121 kPa (17.5 psi), and a gradient of 316.

As can be seen in Figure 91, the introduction of ethylene glycol produced a slight decrease in the permeability of the samples, followed by rising permeabilities which were slow initially then more rapid. The permeabilities peaked before they dropped off slightly to their final equilibrium permeability. Specifically, sample UR-1 reached a peak permeability of 7.8 x 10^{-8} cm/sec after a flow of 4.0 pore volumes on ethylene glycol. Thence the permeability dropped off slightly until it came to an equilibrium at approximately 6.9 x 10^{-8} cm/sec after 5.3 pore volumes of flow of ethylene glycol. That permeability was maintained up to the end of the test, which occurred after a total flow of 10 pore volumes of ethylene glycol. The permeability of sample UR-14 peaked at 4.4 x 10^{-8} cm/sec after 2.5 pore volumes of ethylene glycol flow. This was followed by a gradual decrease in permeability up to 6.0 pore volumes flow of ethylene glycol at which time the sample reached an equilibrium permeability of 2.9 x 10^{-8} cm/sec, which was maintained for another 1.0 pore volume of flow. Sample UR-1 was tested with ethylene glycol for 17 days and for a flow of 10 pore volumes. Sample UR-14 was tested for 36 days and for a flow of 7.0 pore volumes with ethylene glycol.

In comparing the permeability versus pore volume flow curves for the two urethane samples with ethylene glycol, one can clearly see their similarity. Upon the introduction of ethylene glycol, both curves had a net rise in permeability of approximately one order of magnitude. The final equilibrium permeability of sample UR-1 was somewhat higher than that of UR-14, however, the reason for that may be that sample UR-1 had a higher equilibrium permeability with water. Even though there is a difference between the final permeabilities of the two samples, the difference is not considered to be significant.

- Permeability Test of Urethane Grout With a 25% Ethylene Glycol Solution - Phase III

Two urethane grout samples, designated UR-38 and UR-39, were tested with a 25% solution of ethylene glycol in water. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 92 and 93 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample UR-38 was permeated with water for 44.4 days with an accumulated flow of 2.3 pore volumes. Sample UR-39 was tested on water for 57.6 days with an accumulated flow of 9.4 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), and a backpressure of zero and 69.0 kPa (10.0 psi) for UR-38 and UR-39, respectively. A gradient of 517 was used in both tests. The water permeability versus pore volume flow curves show a two-and-a-half fold variation. The curve for UR-38 indicates a water equilibrium permeability of 1.9×10^{-9} cm/sec as compared to 4.9×10^{-9} cm/sec for UR-39.

A 25% ethylene glycol solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at 120.8 kPa (17.5 psi). The backpressure remained at original levels. The gradient was maintained at 517. Sample UR-38 was permeated with chemical for 95.6 days with an accumulated chemical flow of 4.3 pore volumes. Sample UR-39 was permeated with chemical for 93.0 days with a sum chemical flow of 10.5 pore volumes. The samples behaved similarly after the introduction of chemical leachate. Each decreased slightly in permeability to new equilibrium permeabilities of 1.6×10^{-9} cm/sec for UR-38 and 3.1×10^{-9} cm/sec for UR-39. The difference was nearly twofold, much the same as their variation in water baseline permeability.

In order to investigate gradient effects, the gradient of sample UR-38 was reduced fivefold to 100. Net confining pressure and backpressure remained unchanged at 120.8 kPa (17.5) and zero, respectively. With this reduction no variation in permeability was noted. UR-39 was not percolated at a reduced gradient.

- Permeability Test of Urethane Grout With 4N Hydrochloric Acid

Two urethane grout samples, UR-22 and UR-28, were tested with 4N hydrochloric acid. The thicknesses of the samples were 36 and 33 mm, respectively, and both were 75 mm in diameter. Figure 94 shows the permeability versus flow test plots for the two samples.

Before the introduction of hydrochloric acid, the two samples were

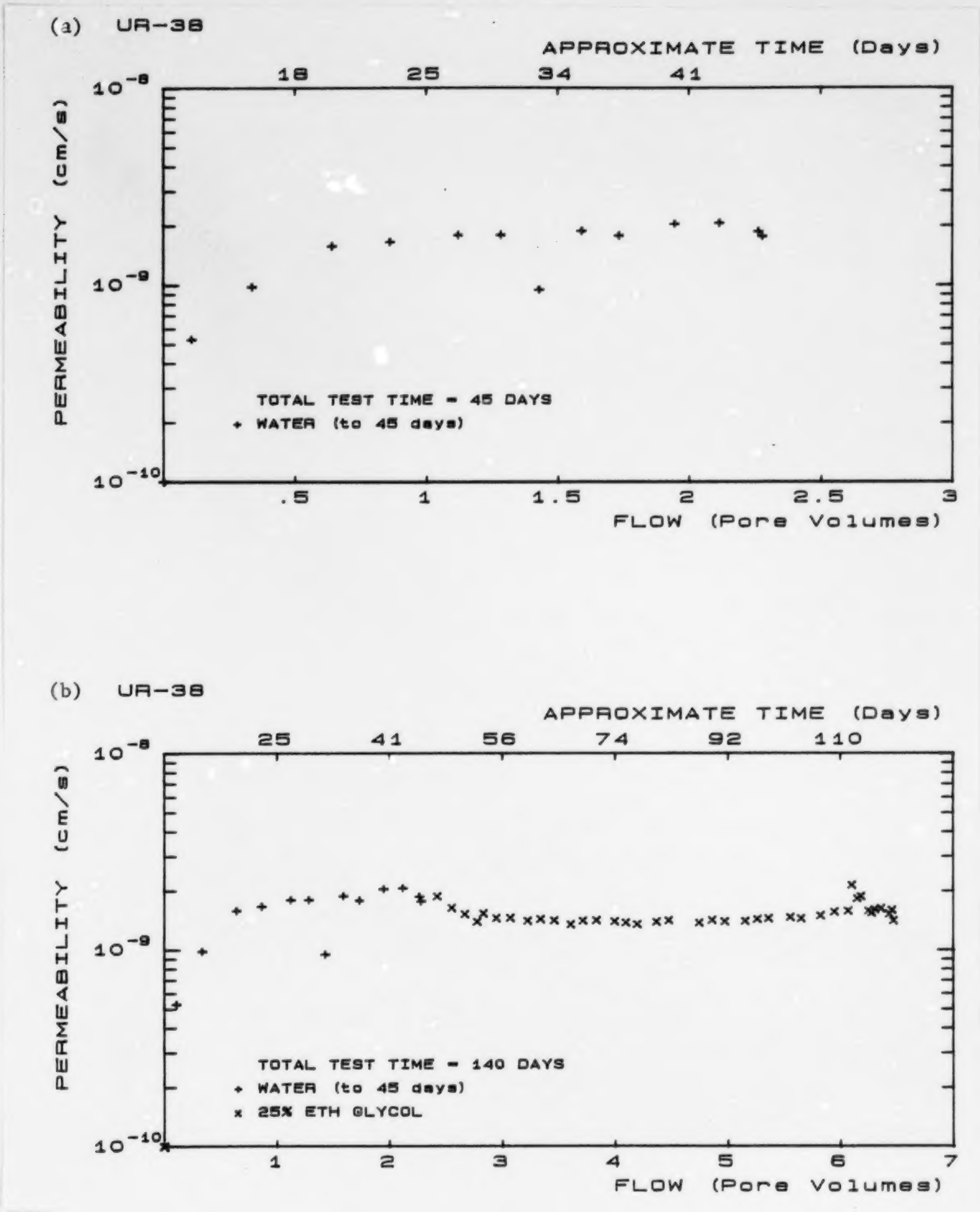


Figure 92. Permeability versus volume of flow through urethane grout sample UR-38. (a) Water as permeant. (b) Water and 25% ethylene glycol as permeants.

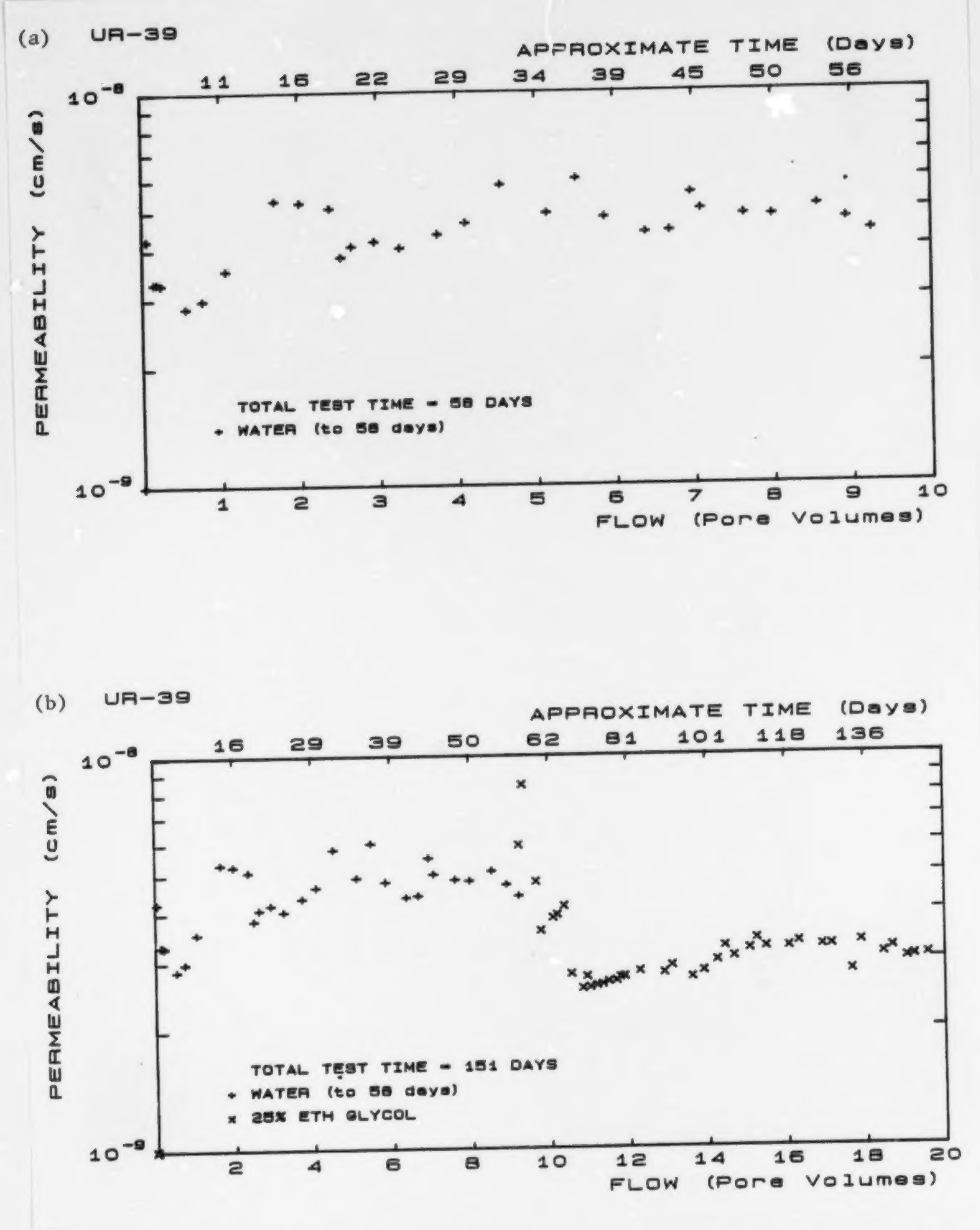


Figure 93. Permeability versus volume of flow through urethane grout sample UR-39. (a) Water as permeant. (b) Water and 25% ethylene glycol as permeants.

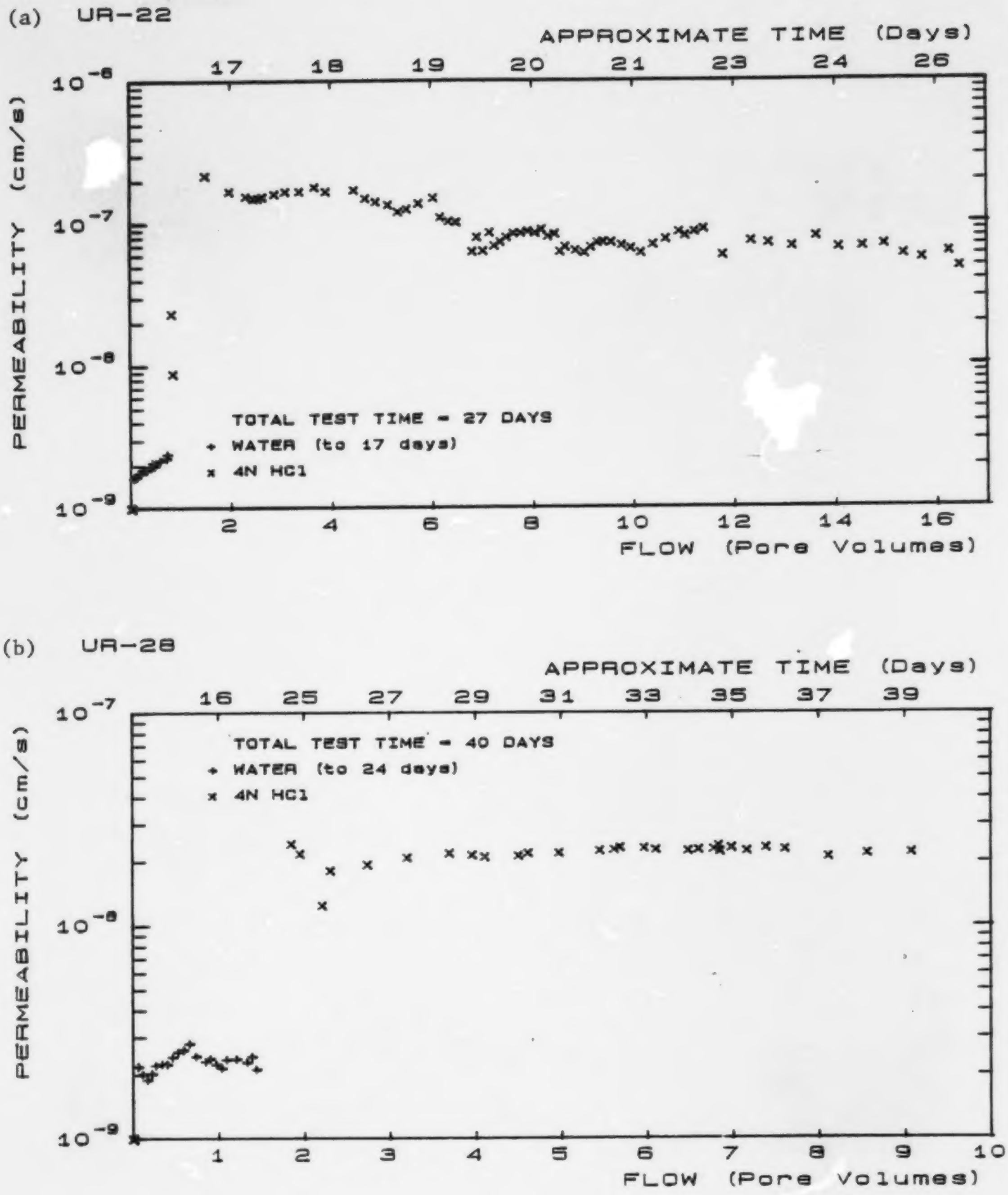


Figure 94. Permeability versus volume of flow of water and 4N hydrochloric acid through urethane grout. (a) Plot for sample UR-22. (b) Plot for sample UR-28.

tested with water in order to saturate them. Sample UR-22 was permeated with water for 17 days, sample UR-28 for 25 days. Both samples were permeated at a headpressure of 173 kPa (25 psi), a tail pressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). Sample UR-22 was tested at a gradient of 293, sample UR-28 at a gradient of 320. Sample UR-22 was taken off of water after a pore volume flow of 0.73 and at a permeability of 2.2 x 10^{-9} cm/sec. Sample UR-28 was taken off the water after a pore volume flow of 1.44 and at a permeability of 1.4 x 10^{-9} cm/sec. It appears that the permeability versus flow curve of sample UR-22 was still rising at the termination of its test with water, while that of sample UR-28 seemed to be in a stable equilibrium at the prestated permeability value.

In the case of sample UR-22, 4N hydrochloric acid was introduced at the same pressure conditions that were used with water, and a gradient of 261. The hydrochloric acid was introduced into sample UR-28 at a reduced headpressure of 104 kPa (15 psi) a tailpressure of 0, a net confining pressure of 121 kPa (17.5), and a gradient of 284. As can be seen in Figure 94, sample UR-22 exhibited an immediate increase in its permeability upon the introduction of hydrochloric acid. Within twelve hours the permeability of the sample rose to a peak value of 2.2 x 10^{-7} cm/sec. This occurred after only 0.8 pore volume of flow with hydrochloric acid. Thereafter, the permeability of the sample gradually decreased to what may be considered a semi-equilibrium state with a permeability of between 6.6 and 7.2 x 10^{-8} cm/sec. This occurred between 7.8 and 13.8 pore volumes of flow of hydrochloric acid. However, the continued testing of the sample with hydrochloric acid resulted in further reductions of permeability, and, at the completion of the test, it had dropped to 4.9 x 10^{-8} after a cumulative flow of 15.8 pore volumes of hydrochloric acid. For this sample, the total testing time with hydrochloric acid was ten days.

Figure 94 shows that the introduction of hydrochloric acid into sample UR-28 caused an immediate one order of magnitude increase in permeability, which peaked at 2.5 x 10^{-8} cm/sec after a pore volume flow of 0.4 and only 18 hours on hydrochloric acid. With continuing testing, the sample reached an equilibrium permeability of approximately 2.2 x 10^{-8} cm/sec. This occurred after 2.6 pore volumes of flow of hydrochloric acid and a test duration of 7 days. The testing with hydrochloric acid continued until 8.1 pore volumes of hydrochloric acid had passed through the sample and 22 days had elapsed. The final equilibrium permeability of the sample was 2.3 x 10^{-8} cm/sec.

In comparing the permeability versus flow curves for the two samples, one notes both similarities and differences. Both samples had increases in their permeabilities due to the introduction of the hydrochloric acid. Sample UR-22 had an increase in its permeability of 1.5 orders of magnitude at its final equilibrium, while sample UR-28 had an increase of one order of magnitude. Consequently, the final equilibrium permeabilities of the two samples differed by as much as half an order of magnitude. One may speculate that the higher equilibrium permeability of sample UR-22 may have been due to its shorter exposure to water, that is, sample UR-22 was tested with water for a flow of 0.73 pore volume, while sample UR-28 was permeated with water for a pore volume flow of 1.44. Even though the results from the two tests do not match, the authors are confident that the two equilibrium permeabilities obtained would bound the real equilibrium permeability of urethane grout with 4N hydrochloric acid.

- Permeability Test of Urethane Grout With a 1N Hydrochloric Acid Solution - Phase III

Two urethane grout samples, designated UR-36 and UR-37, were tested with a 1N solution of hydrochloric acid in water. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 95 and 96 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample UR-36 was permeated with water for 58.2 days with an accumulated flow of 4.1 pore volumes. Sample UR-37 was tested on water for 32.7 days with an accumulated flow of 2.3 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), a backpressure of zero, and a gradient of 517. The water permeability versus pore volume flow curves for UR-36 and UR-37 show little variation compared to one another. The curve for UR-36 indicates a water baseline permeability of 2.4 x 10^{-9} cm/sec as compared to 2.2 x 10^{-9} cm/sec for UR-37.

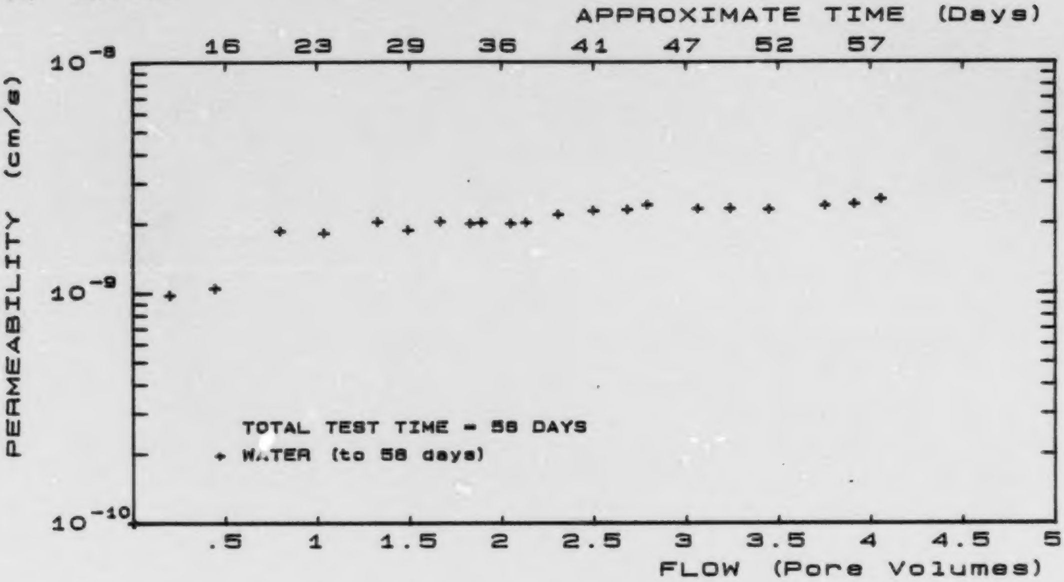
A 1N solution of hydrochloric acid in water was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure, backpressure, and gradient were maintained at the levels set for the test on water. Sample UR-36 was permeated with chemical for 28.3 days with an accumulated chemical flow of 8.1 pore volumes. Sample UR-37 was permeated with a 1N hydrochloric acid solution for 14.4 days with a sum chemical flow of 2.2 pore volumes. Both samples reacted in a similar fashion when the chemical leachate was introduced. Gradual increases of permeability extended over approximately eighteen to twenty-four hours with less than half a pore volume percolating through the samples. Over a period of eight days UR-36 reached an equilibrium permeability of 5.8 x 10^{-8} cm/sec as compared to a similar permeability of 5.0 x 10^{-8} cm/sec for UR-37 over a period of less than three days. The gradients were then decreased to 103 while maintaining the original net confining pressure of 120.8 kPa (17.5 psi) and zero backpressure. The permeability of sample UR-36 decreased slightly to a new equilibrium of 3.6 x 10^{-8} cm/sec, while that of UR-37 increased minimally to 5.4 x 10^{-8} cm/sec.

- Permeability Test of Urethane Grout With 100% Methanol

Figure 97 shows the permeability test plots for the two urethane grout samples tested with 100% methanol. They were designated as UR-11 and UR-13. Both samples were 75 mm in diameter, and their thicknesses were 36 and 29 mm, respectively.

The samples were initially permeated with water to saturate them prior to the introduction of methanol. Sample UR-11 was tested with water for 67 days, sample UR-13 for 39 days. Sample UR-11 was permeated at a headpressure of 104 kPa (15 psi), a tailpressure of 0, a gradient of 293, and an effective confining pressure that, for the most part, was 155 kPa (22.5 psi). The confining pressure was later reduced to 121 kPa (17.5 psi). Sample UR-13 was permeated with water at a headpressure of 173 kPa (25 psi), a tailpressure of

(a) UR-36



(b) UR-36

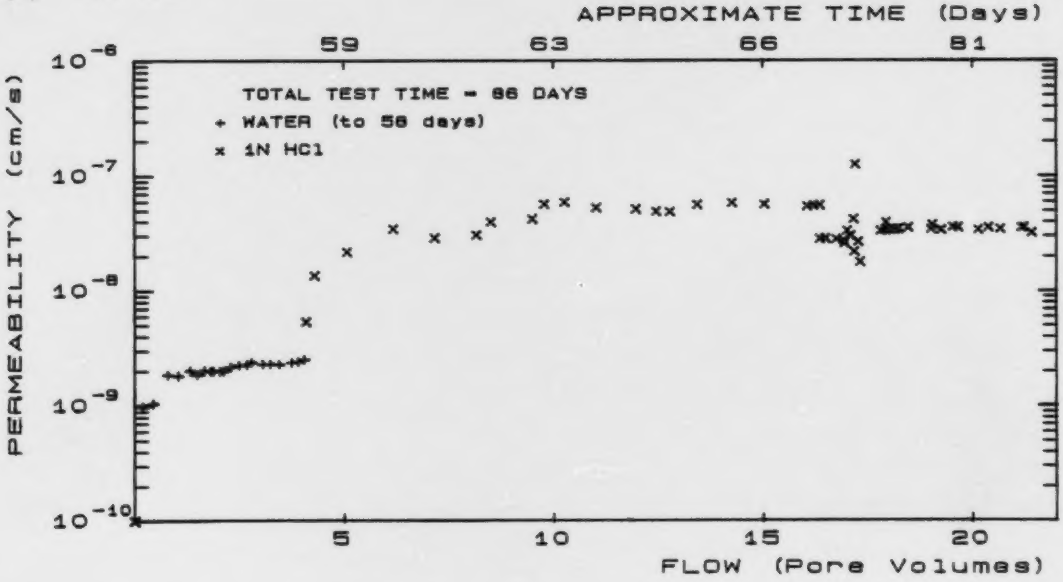


Figure 95. Permeability versus volume of flow through urethane sample UR-36. (a) Water as permeant. (b) Water and 1N hydrochloric acid as permeants.

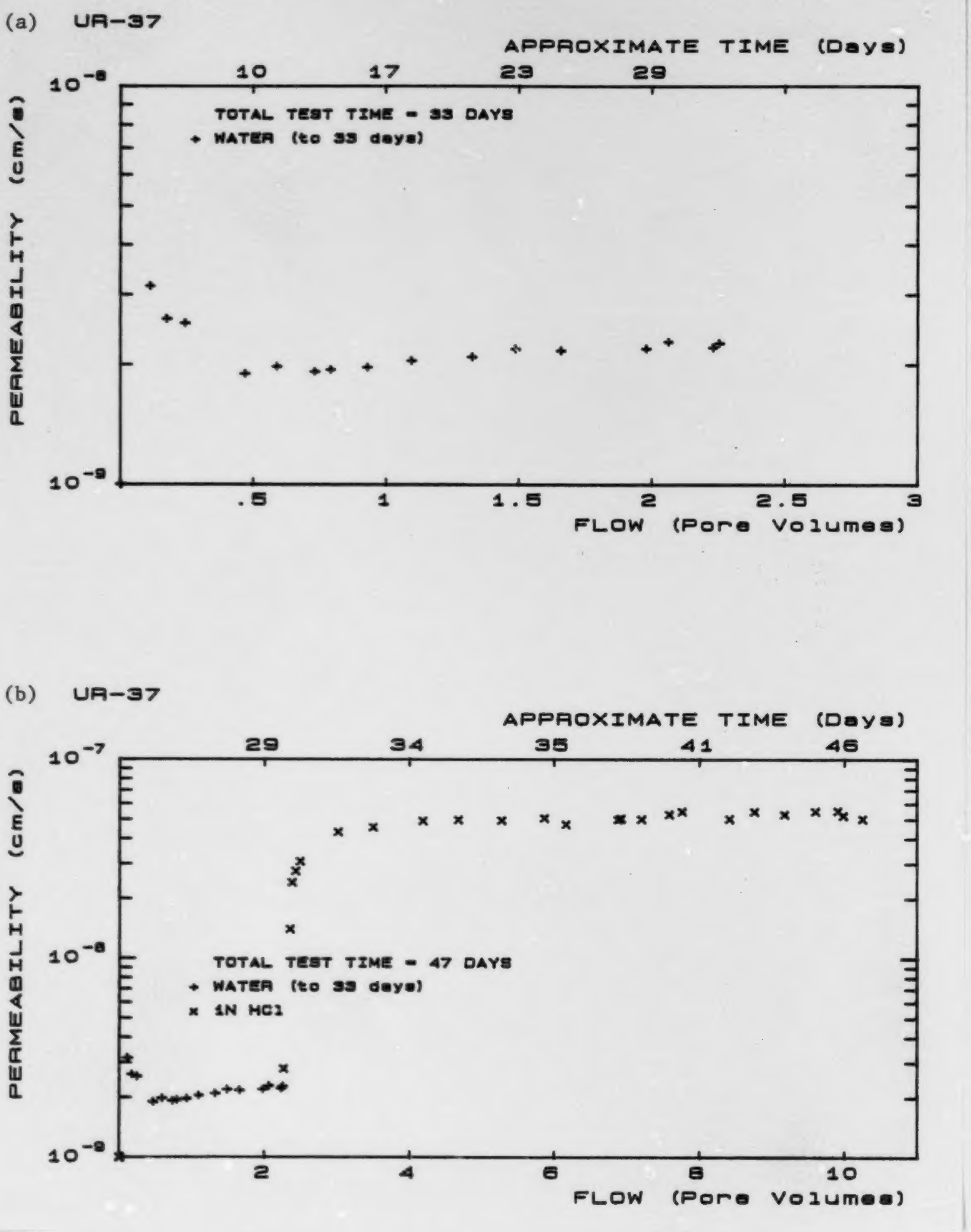
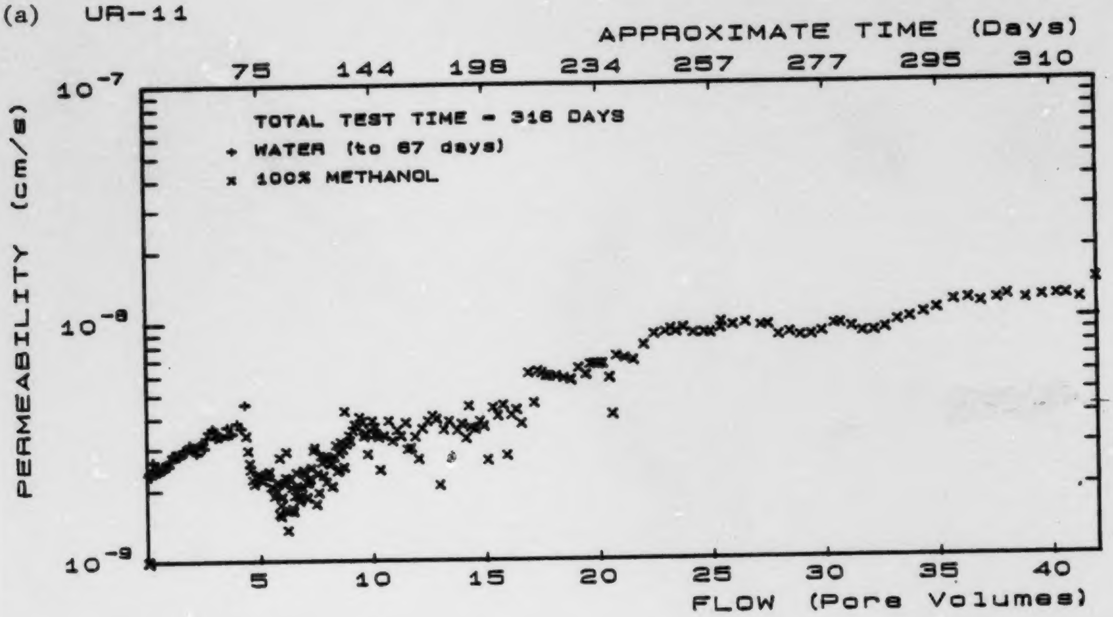


Figure 96. Permeability versus volume of flow through urethane grout sample UR-37. (a) Water as permeant. (b) Water and 1N hydrochloric acid as permeants.

(a) UR-11



(b) UR-13

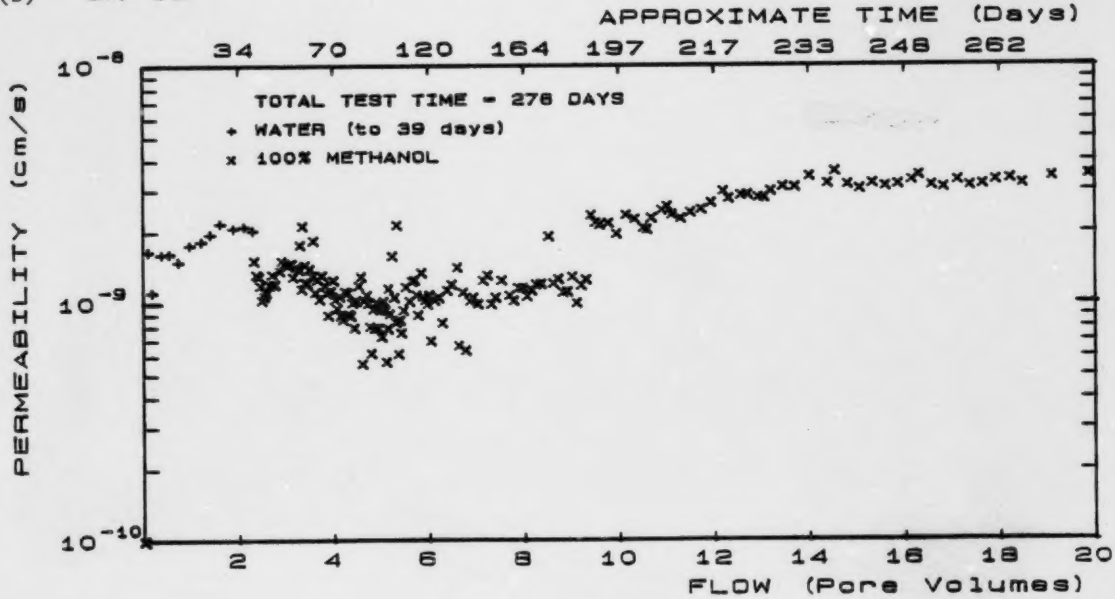


Figure 97. Permeability versus volume of flow of water and 100% methanol through urethane grout. (a) Plot for sample UR-11. (b) Plot for sample UR-13.

69 kPa (10 psi), a confining pressure of 121 kPa (17.5 psi), and a gradient of 364. Sample UR-11 was tested with water until a total flow of 4.4 pore volumes was reached, at which time its permeability was approximately 3.7 x 10^{-9} cm/sec. Even though the permeability versus flow curve for sample UR-11 exhibited a slightly rising tendency on water, the permeability seems to have equilibrated. The permeability of sample UR-13 came to an equilibrium of 2.1 x 10^{-9} cm/sec after 2.3 pore volumes of flow of water.

Methanol was introduced into sample UR-11 at a headpressure of 104 kPa (15 psi) which was increased to 173 kPa (25 psi) after the sample was changed to another testing station. The tailpressure for the beginning half of the testing was set at 0 and was later increased to 69 kPa (10 psi). The effective confining pressure started out at 190 kPa (27.5 psi) and was later reduced to 173 kPa (25 psi) and again to 121 kPa (17.5 psi). The gradient on methanol was for the most part set a 370, except during the first month of testing when it was at 493.

Methanol was introduced into sample UR-13 at a headpressure of 104 kPa (15 psi), a tailpressure of 0, a net confining pressure of 190 kPa (27.5 psi), and at a gradient of 459. The headpressure was later increased to 173 kPa (25 psi) with a simultaneous increase of tailpressure to 69 kPa (10 psi). The confining pressure was reduced to 121 kPa (17.5 psi) but the gradient was maintained at 459.

As can be seen on the permeability versus flow curve for sample UR-11 in Figure 97, upon the introduction of the methanol, the permeability of the sample decreased slightly and then proceeded to rise. This rise was intermittent, in that one can see flow periods over which there was a small rise, followed by a level portion. This phenomenon can be observed repeatedly along the curve. For example, at a pore volume flow of 4.6 on methanol, the permeability seemed to have come to an equilibrium at 3 x 10^{-9} cm/sec, which equilibrium was maintained over 5 pore volumes of flow. This was followed by a rise, an equilibrium, another rise, and again equilibrium until, for example, after 18.5 pore volumes of methanol flow, the permeability came to rest at 9 x 10^{-9} cm/sec. Because of this repeated rise and equilibrium phenomenon, the sample was tested over a very long period--altogether 317 days, out of which 250 were on methanol. After 38 pore volumes of flow of methanol, the terminal equilibrium permeability was 1.25 x 10^{-8} cm/sec.

As shown in Figure 97, sample UR-13 exhibited a permeability versus flow relationship similar to that of sample UR-11. Upon the introduction of methanol, the sample permeability decreased slightly and then began to rise very slowly. After a testing period of 230 days and a total flow of 17.2 pore volumes of methanol, the permeability was still increasing very slowly and reached a value of 3.5 x 10^{-9} cm/sec.

When one compares the permeability versus flow curves in Figure 97, it is noted that the two curves are very similar, especially if the comparison is made at the end of the first 17.5 pore volumes of flow of methanol. It is noted that after this flow the permeability of sample UR-11 was 6.5 x 10^{-9} cm/sec, while that of sample UR-13 was 3.4 x 10^{-9} cm/sec, showing fair agreement. With additional flow the permeability of sample UR-11 continued to rise and, as was described before, it reached a level of 1.25 x 10^{-8} cm/sec. This is considered the ultimate value of the permeability of urethane grout with 100% methanol.

- Permeability Test of Urethane Grout With Real-Site Paint Waste

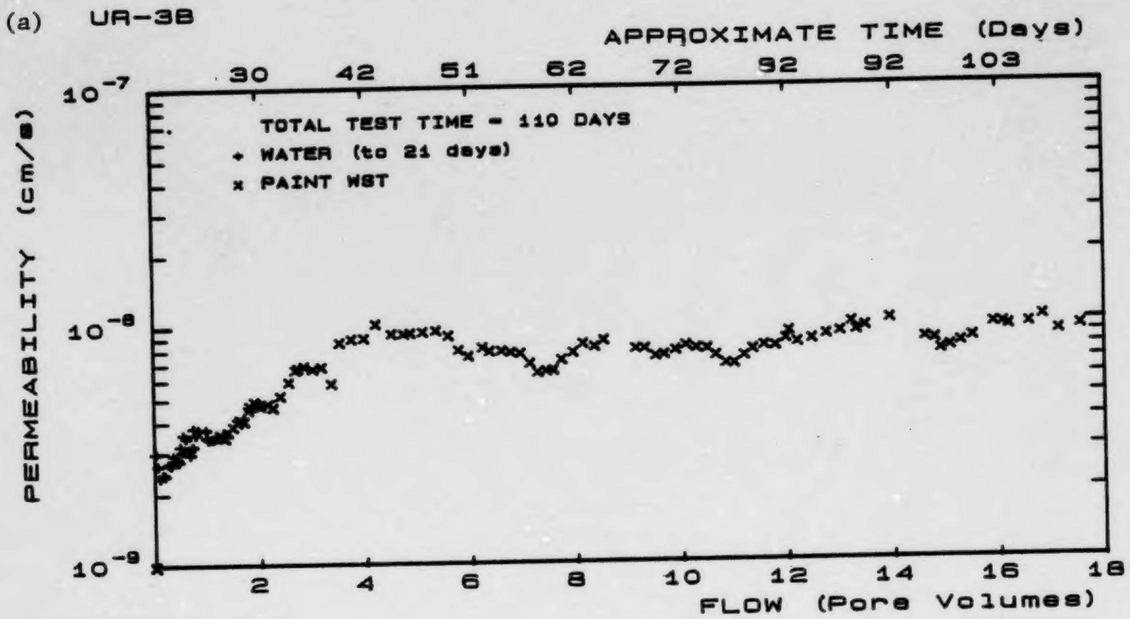
Two urethane grout samples, UR-3B and UR-4B, were tested with real-site paint waste. The sample thicknesses were 43 and 45 mm, respectively, and both samples were 75 mm in diameter. Figure 98 shows the permeability versus pore volume flow curves for the two samples.

Sample UR-3B was first permeated with water for 22 days. Water was introduced into the sample at a headpressure of 138 kPa (20 psi), a backpressure of zero, a net confining pressure of 138 kPa (20 psi), and at a gradient of 327. Fourteen days into the test, the backpressure was increased to 34.5 kPa (5 psi), which in turn dropped the net confining pressure to 121 kPa (17.5 psi) and the gradient to 245. With water as the permeant, the permeability of the sample first rose to 3.9 x 10^{-9} cm/sec, then dropped to an equilibrium permeability of 3.5 x 10^{-9} cm/sec after 1.2 pore volumes of flow.

Sample UR-4B was saturated with water at a headpressure of 138 kPa (20 psi), a backpressure of zero, a net confining pressure of 138 kPa (20 psi), and a gradient of 313. The permeability versus flow curve peaked at 8.3 x 10^{-9} cm/sec then dropped down to an equilibrium value of 5.6 x 10^{-9} cm/sec, after 3.5 pore volumes of water flow and 31 days of testing.

The paint waste was introduced into sample UR-3B at a headpressure of 138 kPa (20 psi), a backpressure of zero, a net confining pressure of 138 kPa (20 psi), and at a gradient of 327. After nine days, however, the headpressure was increased to 175 kPa (25 psi), which in turn increased the net confining pressure to 155 kPa (22.5 psi) and the gradient to 409. With the introduction of paint waste, the permeability versus pore volume of flow curve started a gradual rise, followed by a more slowly rising portion which ended with the permeability reaching 9.8 x 10^{-9} cm/sec after 4.2 pore volumes and 28 days of testing with paint waste. Thence the permeability versus pore volume flow curve dropped to a permeability of 6.5 x 10^{-9} cm/sec, and, with continued rises and drops, very slowly rose to a final equilibrium permeability of 9.8 x 10^{-9} cm/sec, or a 0.6 order of magnitude rise above its permeability with water. This sample was tested with paint waste for a total of 88 days.

The paint waste was first introduced into sample UR-4B at a headpressure of 138 kPa (20 psi), a backpressure of 0, a net confining pressure of 138 kPa (20 psi), and with a gradient of 313. After eight days on paint waste, the headpressure was increased to 173 kPa (25 psi), which in turn increased the net confining pressure to 155 kPa (22.5 psi) and the gradient to 391. With the introduction of paint waste the permeability versus pore volume flow curve for the sample rose gradually to a first plateau of permeability equal to 1.1 x 10^{-8} cm/sec after an accumulated pore volume flow of 1.1 and nine days of testing with paint waste. Continued testing caused the permeability to rise again and then to level off at a value of 1.4 x 10^{-8} cm/sec after 4.1 pore volumes of flow and 21 days with paint waste. This was followed



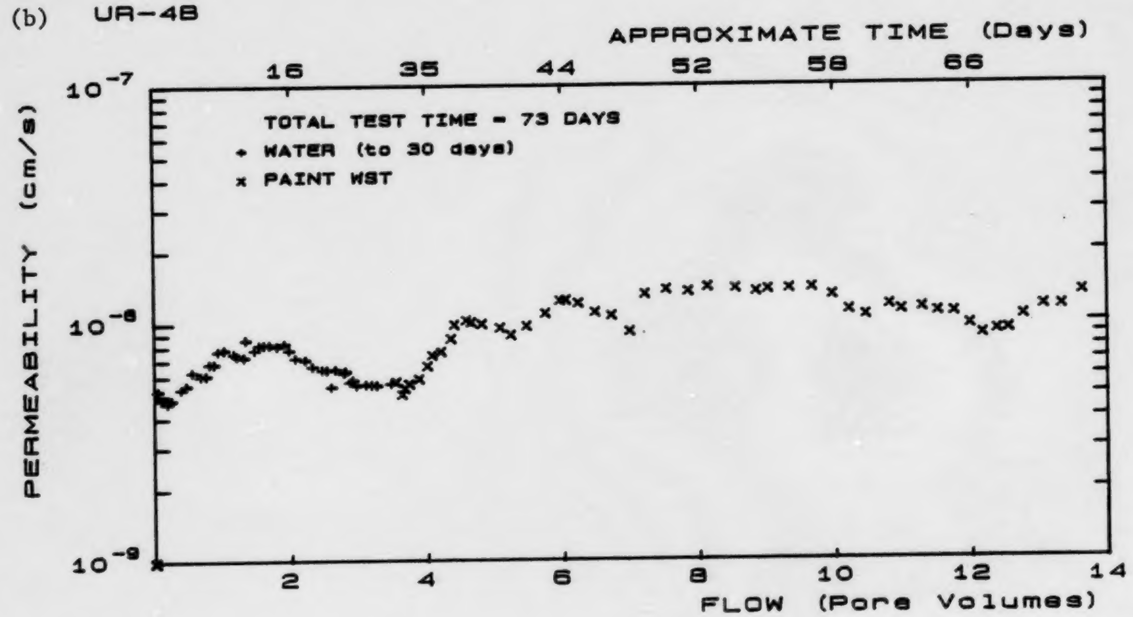


Figure 98. Permeability versus volume of flow of water and real-site paint waste through urethane grout. (a) Plot for sample UR-3B. (b) Plot for sample UR-4B.

by an uneven segment in the curve during which the permeability dropped, then recovered. Sample UR-4B came to an equilibrium permeability of 1.36 x 10^{-8} cm/sec after 42 days and 10.2 accumulated pore volumes of flow of paint waste.

As shown in Figure 98 the two permeability versus pore volume flow curves on paint waste are quite similar, with the final equilibrium permeabilities being very close. It can be seen that the paint waste had a relatively small effect on the permeability of urethane grout, causing only between 0.5 and 0.6 order of magnitude increase in its permeability.

- Permeability Test of Urethane Grout With Real-Site Refinery Waste

Two urethane grout samples, UR-5B and UR-6B, were tested with real-site refinery waste. Their thicknesses were 37 and 29 mm, respectively, and both were 75 mm in diameter. Figure 99 shows the permeability versus pore volume flow plots for the samples.

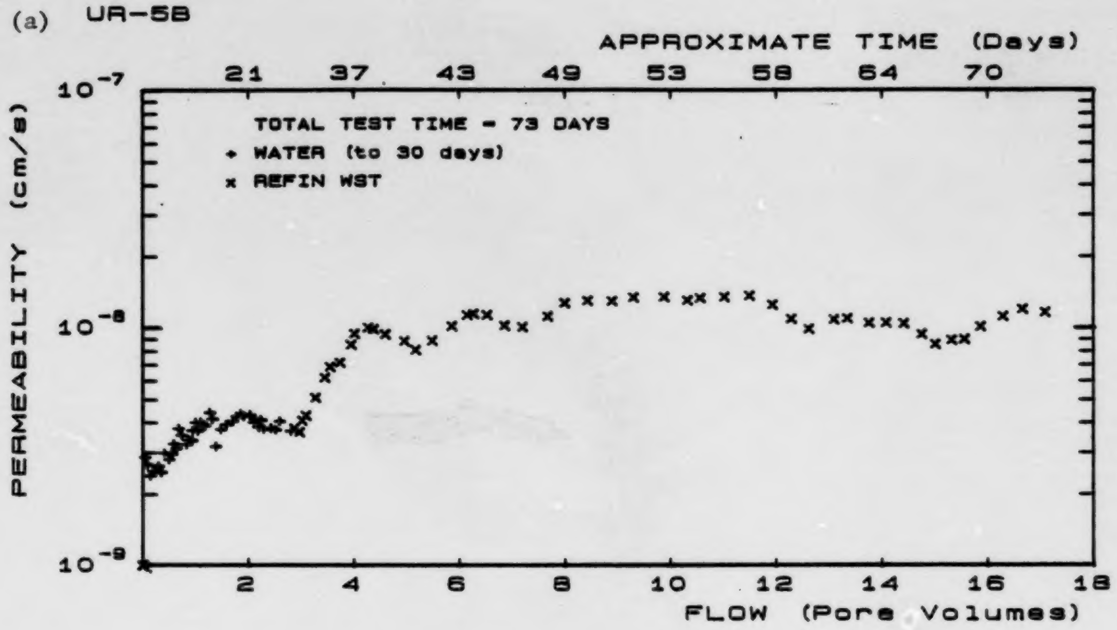
Preceding the introduction of refinery waste, the two samples were saturated with water. The water permeation through both samples was accomplished at a net confining pressure and headpressure of 138 kPa (20 psi), and a backpressure of zero. Sample UR-5B was tested with water at a gradient of 380 for 30 days and 2.8 pore volumes of flow, while sample UR-6B was permeated with water for 31 days, to an accumulated flow of 4.8 pore volumes, and at a gradient of 485. Sample UR-5B equilibrated with water at a permeability of 4 x 10^{-9} cm/sec, sample UR-6B at 3.6 x 10^{-9} cm/sec.

The refinery waste was introduced into both samples at pressure conditions and gradients identical to those used with water. After eight days, the headpressure for both samples was increased to 173 kPa (25 psi), which resulted in an increase in the net confining pressure to 155 kPa (22.5 psi). The gradient for sample UR-5B was increased to 475 while the gradient for sample UR-6B was increased to 607.

The introduction of refinery waste into sample UR-5B caused a fairly quick rise of 0.6 order of magnitude in the permeability of the sample to a value of 1 x 10^{-8} cm/sec after a refinery waste flow of just 1.5 pore volumes and a test duration of 8 days. There was a downturn in the permeability when the headpressure was incremented; however, the trend of the permeability was to slowly rise with continued flow to an equilibrium value of 1.4 x 10^{-8} cm/sec. With further testing the permeability dropped off slightly to 1.1 x 10^{-8} cm/sec and remained there for the rest of the test. The permeability test on refinery waste took 43 days and resulted in a total of 14.3 pore volumes of refinery waste flow.

Upon the introduction of refinery waste into sample UR-6B, its permeability rose quickly to 1.1 x 10^{-8} cm/sec after a refinery waste flow of 2.7 pore volumes over a period of 9 days. This was followed by a relatively brief downturn in permeability. With continued testing the permeability rose again and peaked at 1.2 x 10^{-8} cm/sec, followed by some erratic permeability versus flow readings, ending at a final equilibrium permeability of 1.1 x 10^{-8} cm/sec after 41 days and a total flow of 21 pore volumes with refinery waste.

(a)



(b)

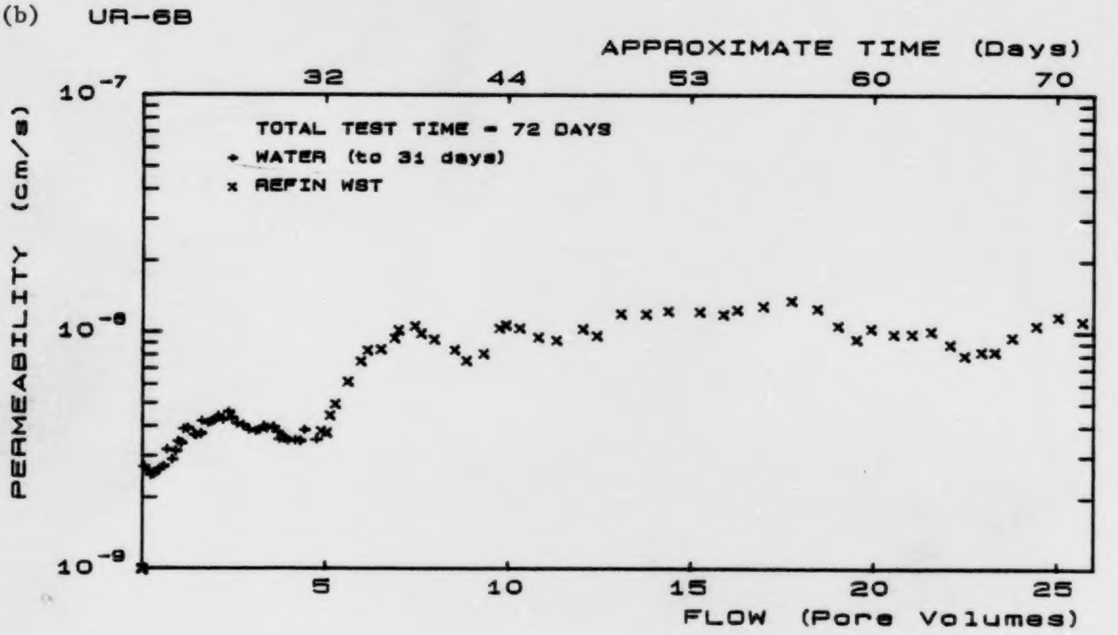


Figure 99. Permeability versus volume of flow of water and real-site refinery waste through urethane grout. (a) Plot for sample UR-5B. (b) Plot for sample UR-6B.

In comparing the two permeability versus flow curves of the urethane samples with refinery waste, it appears that the two curves are very similar and the final permeability values are very close. It is clear that the introduction of refinery waste into urethane samples had relatively little effect on their permeability. The average increase in the permeabilities above those which were obtained with water was between 0.6 and 0.75 order of magnitude.

- Permeability Test of Urethane Grout With 25% Sodium Hydroxide

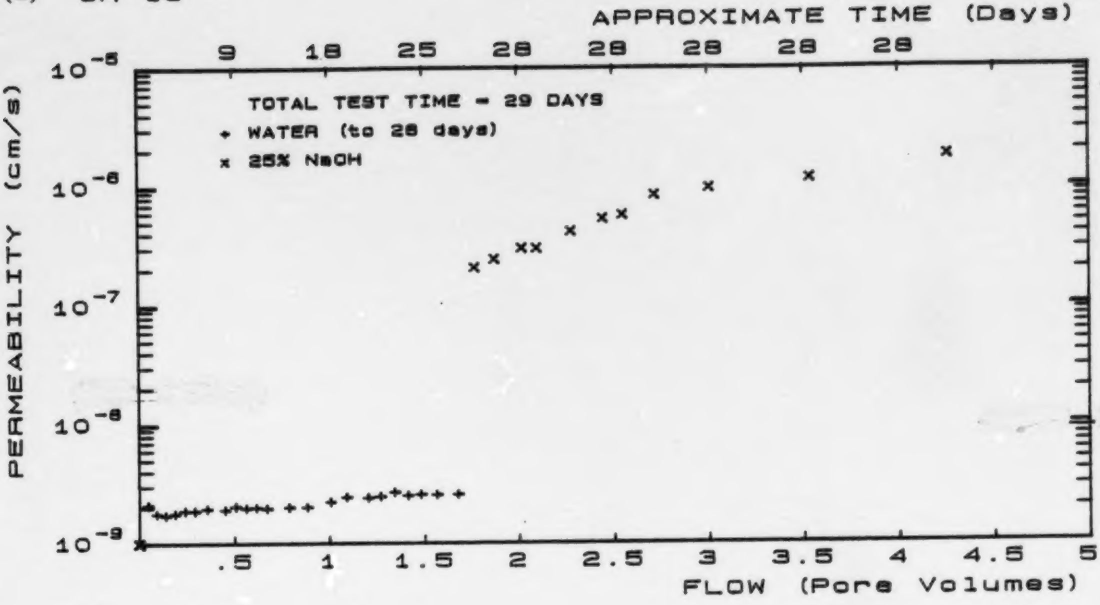
Two urethane grout samples, UR-19 and UR-23, were tested with 25% sodium hydroxide. Their thicknesses were 32 and 36 mm, respectively, and both were 75 mm in diameter. Figure 100 shows the permeability versus pore volume flow plots for the two samples.

Preceding the introduction of 25% sodium hydroxide, the two samples were saturated with water. Water was permeated through both samples with a headpressure of 173 kPa (25 psi) and a tailpressure of 69 kPa (10 psi). This was accomplished at a net confining pressure of 121 kPa (17.5 psi) for sample UR-23. For sample UR-19, the test was started at a net confining pressure of 121 kPa (17.5 psi), which was later reduced to 86 kPa (12.5 psi). Sample UR-19 was permeated with water at a gradient of 330 for 29 days and to a total of 1.7 pore volumes of flow, while sample UR-23 was tested with water for 15 days with an accumulated flow of 0.7 pore volume at a gradient of 293. For sample UR-19 the permeability equilibrated at 2.6 x 10^{-9} cm/sec. For sample UR-23 the equilibrium permeability with water was 2.3 x 10^{-9} cm/sec. Both samples exhibited a fairly level permeability versus flow curve with water.

The 25% sodium hydroxide was introduced into both samples at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). Gradients of 259 and 230 were used with samples UR-19 and UR-23, respectively. After the introduction of sodium hydroxide, the permeabilities of both samples started to rise immediately. The permeability of sample UR-19 increased to 1.1 x 10^{-6} cm/sec, nearly a three orders of magnitude increase within half an hour of testing, with a pore volume flow of only 0.5. The permeability of sample UR-19 reached its first plateau at a permeability of 1.6 x 10^{-6} cm/sec after a pore volume flow of 1.8 with sodium hydroxide. As can be seen in Figure 100, the permeability continued to rise slightly with further flow and peaked at the permeability of 3 x 10^{-6} cm/sec after an accumulated 45 pore volumes of sodium hydroxide flow.

Sample UR-23 also showed a sharp initial increase in its permeability with sodium hydroxide, when its permeability jumped from 2.3 x 10^{-9} to 9.4 x 10^{-8} cm/sec after one and one-half hours and with a sodium hydroxide flow of 0.12 pore volume. Following that, the rise in permeability continued at a slower rate. The sample reached a plateau in its permeability at 1.2 x 10^{-6} cm/sec after an accumulated pore volume flow of 3.0 with sodium hydroxide. This was followed by a further gradual rise in permeability, which reached a maximum of 5.3 x 10^{-6} cm/sec at the end of the test after an accumulated sodium hydroxide flow of 5.6 pore volumes. The durations of the tests with sodium

(a) UR-19



(b) UR-23

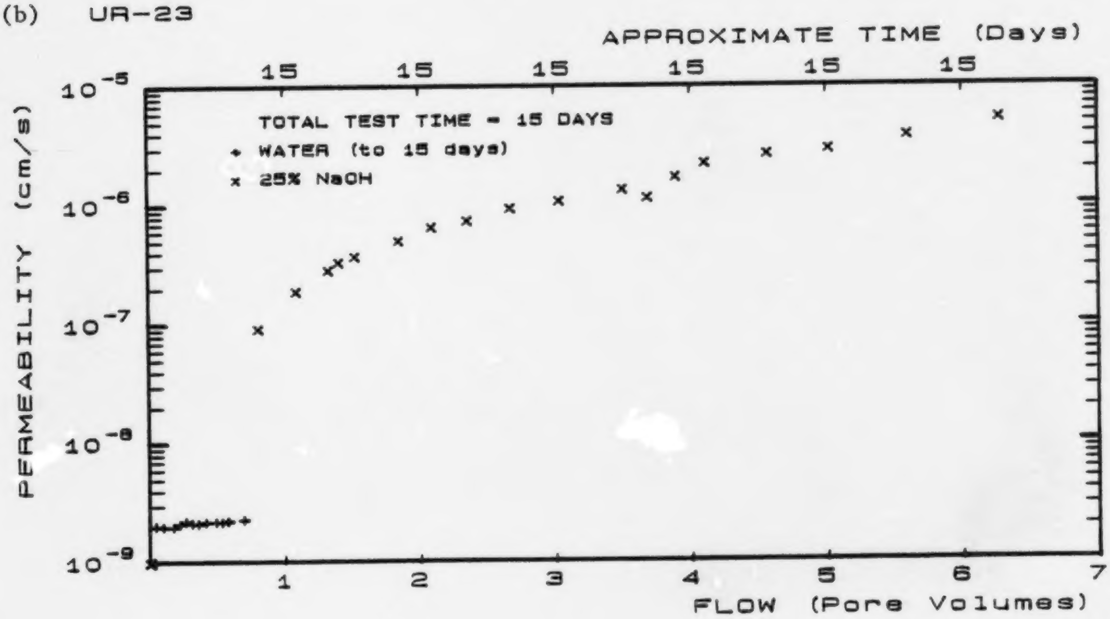


Figure 100. Permeability versus volume of flow of water and 25% sodium hydroxide through urethane grout. (a) Plot for sample UR-19. (b) Plot for sample UR-23.

hydroxide were a little more than five hours for sample UR-19, and a little less than 12 hours for sample UR-23.

It should be noted that the permeability versus pore volume flow curve of sample UR-19 exhibited a drop in permeability toward the end of the test, which was followed by a continuous gradual rise. The drop was due to a brief stoppage in the testing which lasted a little more than half an hour, during which time the pressures were released. It is believed that, had the testing been continued, the permeability of the sample would have again reached the previous peak value. It is noted that the basic shape of the two permeability versus flow curves is very similar. Both samples were tested with sodium hydroxide over an extended pore volume flow, namely, 6.2 for sample UR-19 and 5.6 for sample UR-23. Normally, this extent of testing would have been sufficient; however, as it turned out, equilibrium permeability was not established for either of the two samples. In phase III, two more urethane samples (UR-44 and UR-45) were tested, as described in the following section. These samples were tested over a longer period of time and with accumulated flows of 28 and 40 pore volumes, respectively, and reached one to two orders of magnitude higher final equilibrium permeabilities than samples UR-19 and UR-23.

- Permeability Test of Urethane Grout With a 25% Sodium Hydroxide Solution - Phase III

Two urethane grout samples, designated UR-44 and UR-45, were tested with a 25% solution of sodium hydroxide in water. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 101 and 102 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample UR-44 was permeated with water for 28.5 days with an accumulated flow of 1.9 pore volumes. Sample UR-45 was tested on water for 19.9 days with an accumulated flow of 1.0 pore volume. The testing of the samples was conducted with a net confining pressure of 120.8 and 141.5 kPa (17.5 and 35.0 psi) for UR-44 and UR-45, respectively, a backpressure of zero, and a gradient of 517. The water permeability versus pore volume flow curves for UR-44 and UR-45 show little variation compared to one another after the passage of 0.3 pore volume of water. The curve for UR-44 indicates an equilibrium permeability of 1.9 x 10^{-9} cm/sec as compared to 1.6 x 10^{-9} cm/sec for UR-45.

A 25% sodium hydroxide solution was used as the chemical leachate for this pair of samples. When the chemical was introduced the pressures and gradients were maintained at the same levels as were set in the tests with water. Sample UR-44 was permeated with chemical for 3.1 days with an accumulated chemical flow of 28.3 pore volumes. Sample UR-45 was permeated with chemical for 0.2 day with a sum chemical flow of 32.2 pore volumes. Initial permeability plateaus for the two samples varied by more than one order of magnitude. Sample UR-44 had a permeability of 1.2 x 10^{-4} cm/sec as opposed to 3.4 x 10^{-5} cm/sec for UR-45. The gradient for UR-44 was then decreased to 103 with a net confining pressure at 120.8 kPa (17.5 psi) and a zero backpressure. The permeability reduced to a new equilibrium level of 6.6 x 10^{-5} cm/sec. The leachate/grouted soil reaction for sample UR-45 was quite

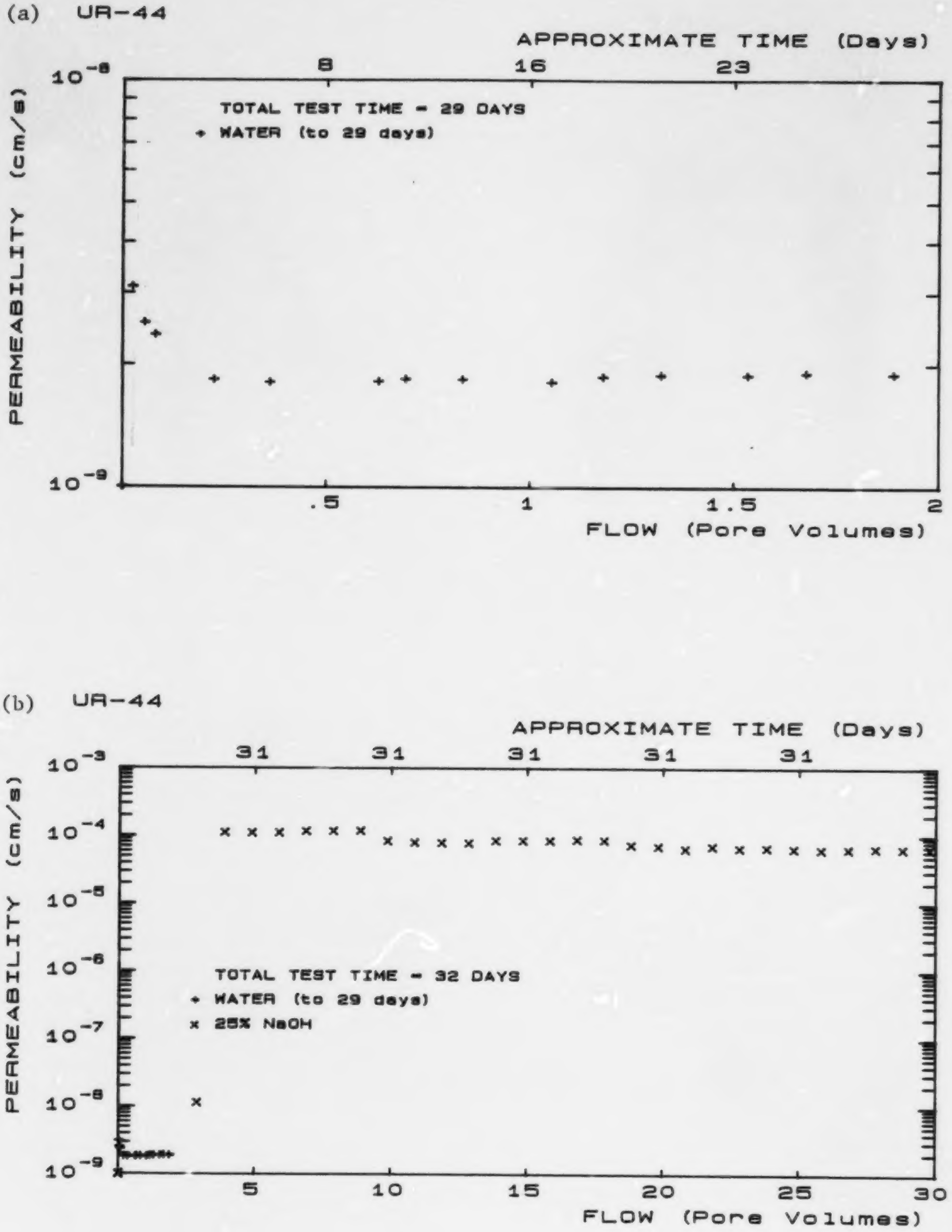


Figure 101. Permeability versus volume of flow through urethane grout sample UR-44. (a) Water as permeant. (b) Water and 25% sodium hydroxide as permeants.

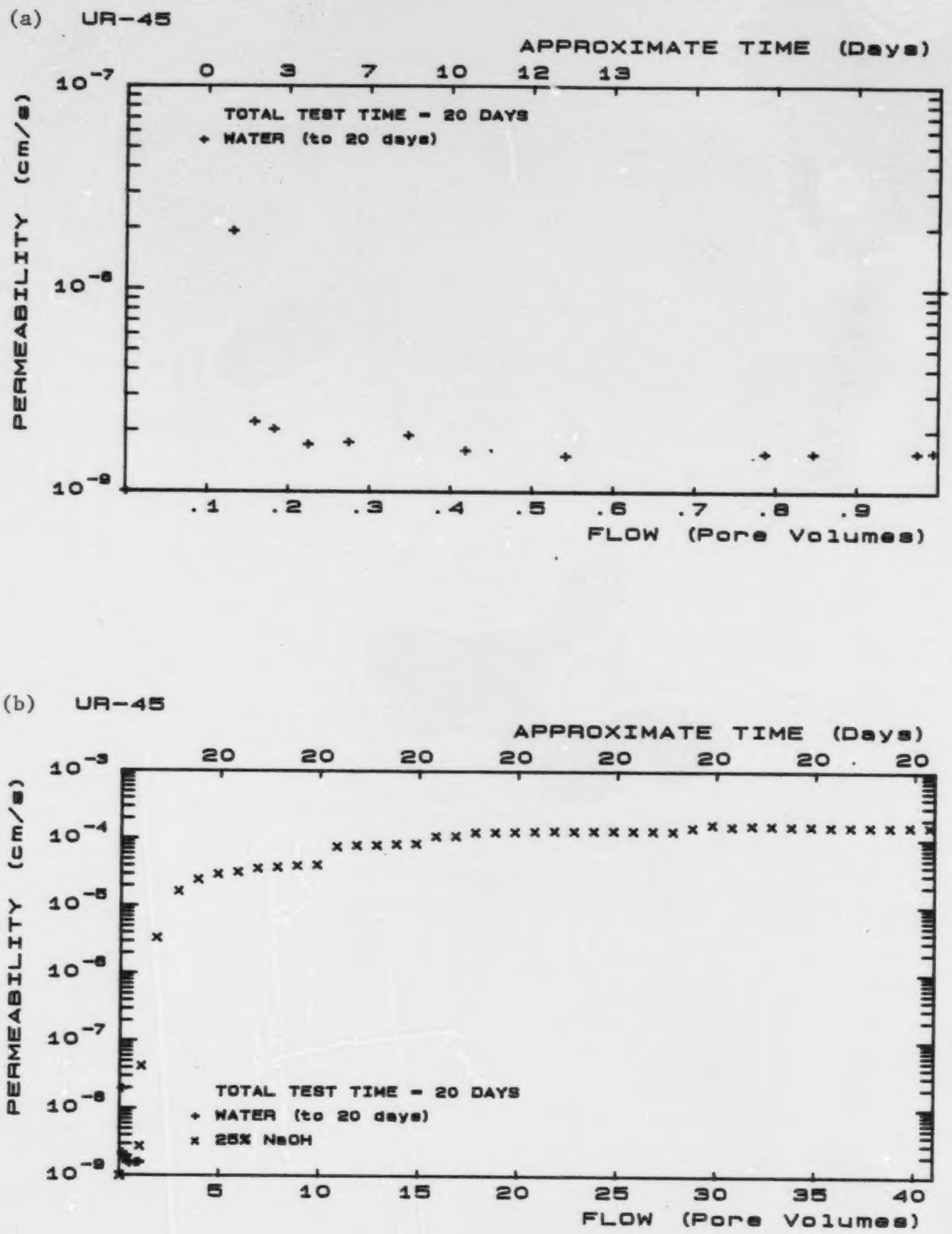


Figure 102. Permeability versus volume of flow through urethane grout sample UR-45. (a) Water as permeant. (b) Water and 25% sodium hydroxide as permeants.

different. An equilibrium permability of 1.4 x 10^{-4} cm/sec was obtained with a gradient of 517. Concurrently, after approximately 0.8 pore volume of chemical flow, the effluent precipitated white particles in suspension (approximately #200 sieve size particles). However, the effluent was gradually cleared of the particles until none was detected after passing approximately 4 pore volumes. The leachate had a yellowish tint throughout the remaining percolation process. A reduction in the gradient to 103 yielded an equilibrium permeability of 1.6 x 10^{-4} cm/sec, a negligible increase in the permeability of the sample.

Sample UR-44 did not precipitate particles in suspension as did UR-45. The reasons are not fully known but one hypothesis can be cited. Chemical "residue" (a possible by-product of the grout gellation process) could be a required component in the precipitation reaction. There could be a potential for the "residue" to be washed from the sample during permeation with water. UR-44 was permeated on water for a longer period of time and a pore volume flow double that of UR-45. Therefore, the potential for total washout of the "residue" was much higher for UR-44 and residue may not have existed when the 25% solution of sodium hydroxide in water was introduced as the permeant.

- Permeability Test of Urethane Grout With a 10% Sodium Hydroxide Solution - Phase III

Two urethane grout samples, designated UR-40 and UR-41, were tested with a 10% solution of sodium hydroxide in water. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 103 and 104 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample UR-40 was permeated with water for 40.9 days with an accumulated flow of 5.6 pore volumes. Sample UR-41 was tested on water for 20.0 days with an accumulated flow of 2.0 pore volumes. The testing of each sample was conducted with a net confining pressure of 120.8 kPa (17.5 psi), a backpressure of zero, and a gradient of 517. The plots of permeability versus flow show approximately a two-fold variation in permeability between the samples. The curve for sample UR-40 indicates an equilibrium permeability of 3.8 x 10^{-9} cm/sec as compared to 2.0 x 10^{-9} cm/sec for UR-41.

A 10% sodium hydroxide solution in water was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure, backpressure and gradient remained at 120.8 kPa, 0, and 517, respectively. Sample UR-40 was permeated with chemical for 0.08 day with an accumulated chemical flow of 36.2 pore volumes. Sample UR-42 was permeated with a 10% solution of sodium hydroxide in water for 0.13 day with a sum chemical flow of 40.4 pore volumes. Both samples experienced an abrupt increase in permeability when the chemical leachate was introduced.

The initial permeability plateaus varied by one order of magnitude. Sample UR-40 had an initial permeability plateau of 1.6 x 10^{-6} cm/sec as compared to 1.6 x 10^{-5} cm/sec for UR-41. Due to the increase in permeability the percolation process had to be run intermittently. Both samples had seven percolation periods with varying rest periods, generally one to three days, in

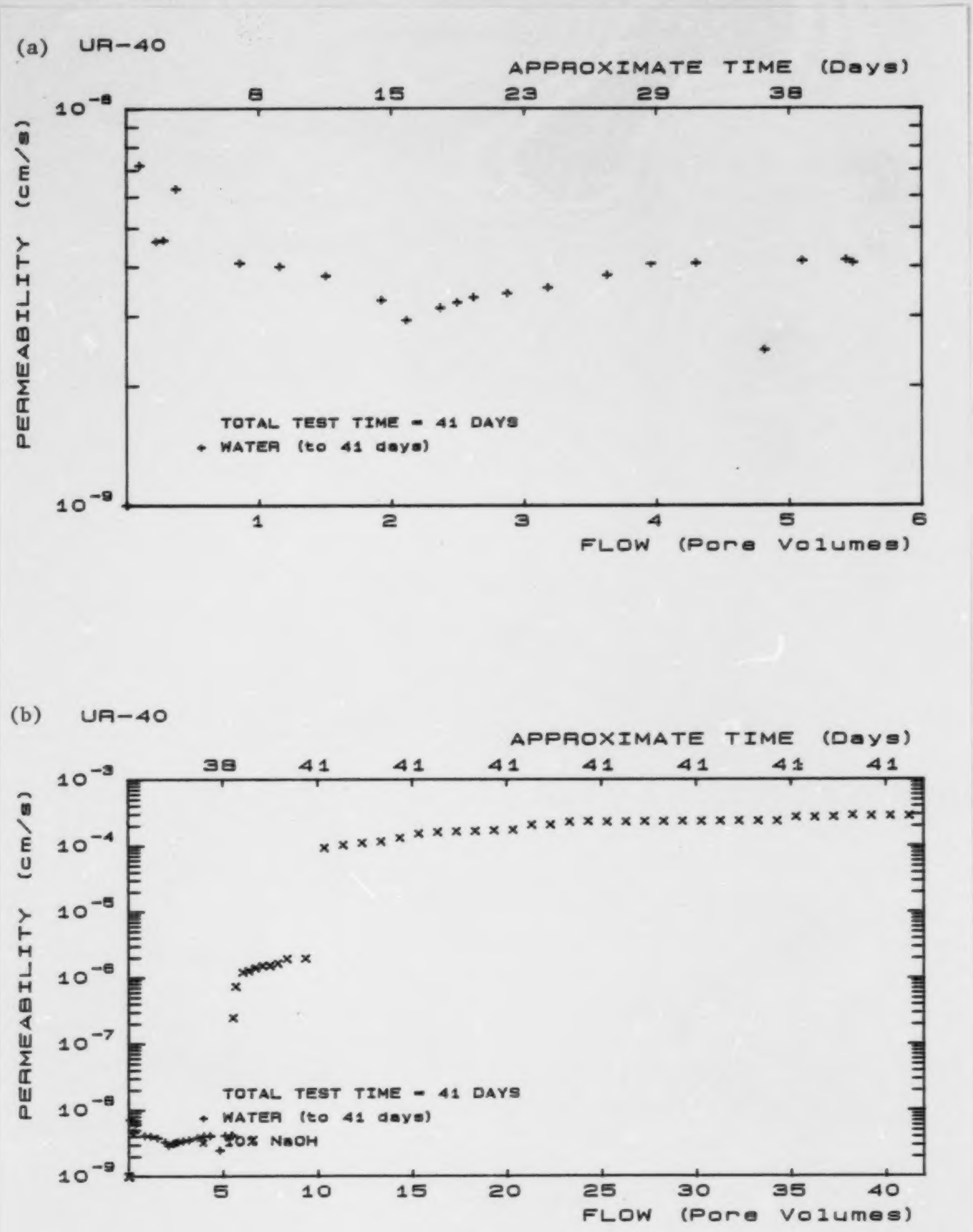


Figure 103. Permeability versus volume of flow through urethane grout sample UR-40. (a) Water as permeant. (b) Water and 10% sodium hydroxide as permeants.

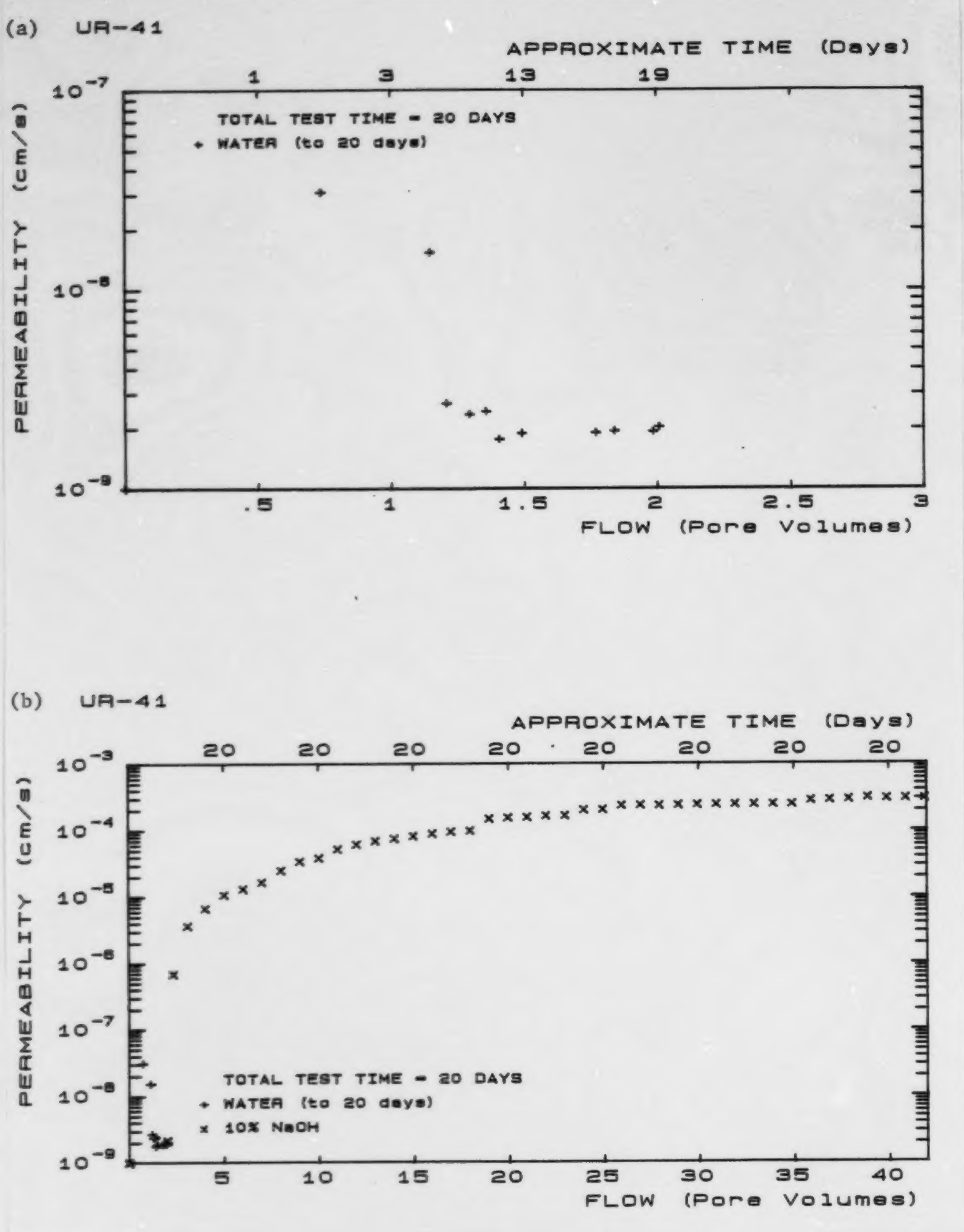


Figure 104. Permeability versus volume of flow through urethane grout sample UR-41. (a) Water as permeant. (b) Water and 10% sodium hydroxide as permeants.

between. The permeabilities increased gradually except for the nearly two order magnitude jump in sample UR-40 after the establishment of its initial permeability plateau. The near identical equilibrium permeabilities of 2.4 x 10^{-4} and 2.5 x 10^{-4} cm/sec for UR-40 and UR-41, respectively, were reached after 29 and 33 pore volumes of the leachate had passed through the respective samples. Thereafter the gradients were reduced to 103 for the last two percolation periods. The net confining pressure and backpressure levels remained unchanged. The permeabilities increased minimally to 2.9 x 10^{-4} cm/sec for UR-40 and to 3.0 x 10^{-4} cm/sec for UR-41.

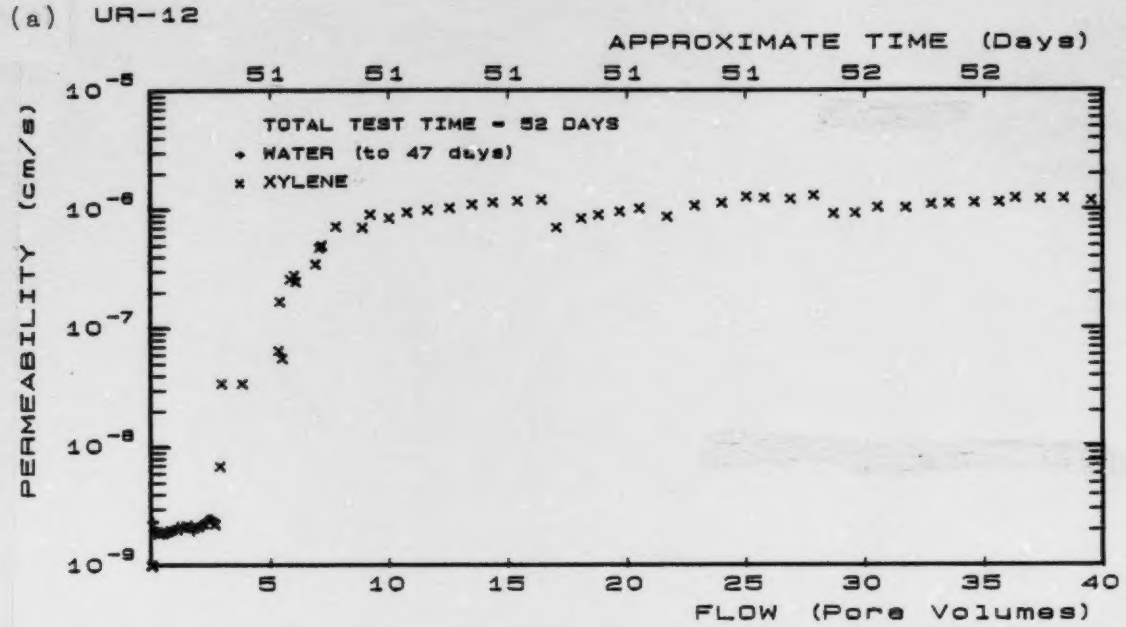
The chemical leachate/grouted soil interaction of the two samples was quite different. White particles (approximately of #200 sieve size) were precipitated in the effluent of UR-41 after one pore volume of flow. After the passage of another nine pore volumes, the effluent cleared and remained so throughout the remainder of the percolation process. Sample UR-40 did not demonstrate this behavior. The reasons for this difference are not fully known but one hypothesis can be cited. Chemical "residue" (a possible by-product of the grout gellation process) could be a required component in the precipitation reaction. There could be potential for the "residue" to be washed from the sample during permeation with water. UR-40 was permeated with water for a longer period of time and a pore volume flow of almost triple that of UR-41. Therefore, the potential for total washout of the "residue" was much higher in sample UR-40. The necessary "residue" may not have existed when the 10% solution of sodium hydroxide in water was introduced as the permeant.

- Permeability Test of Urethane Grout With Xylene

Three urethane grout samples, UR-8, UR-12, and UR-15, were tested with xylene. The thicknesses of samples UR-12 and UR-15 were 33 and 37 mm, respectively, and both were 75 mm in diameter. Figure 105 shows the permeability versus pore volume flow plots for these two samples. The test of sample UR-8 was not conducted long enough on xylene; nevertheless, the results are presented in Figure 106 for comparison.

The testing of samples UR-12 and UR-15 started out with water in order to saturate them. Sample UR-12 was permeated with water at a headpressure of 104 kPa (15 psi), a backpressure of zero, and an effective confining pressure that started out at 155 kPa (22.5 psi) and was later dropped to 121 kPa (17.5 psi). The gradient was maintained at 325. The permeability of the sample started out at 2 x 10^{-9} cm/sec and gradually increased to an equilibrium value of 2.5 x 10^{-9} cm/sec over a period of 48 days with a total water flow of 2.6 pore volumes.

Sample UR-15 was presaturated with water at a headpressure of 173 kPa (25 psi), a tailpressure of 69 kPa (10 psi), and a net confining pressure of 121 kPa (17.5 psi). The gradient of permeation was 285. Its permeability versus pore volume flow curve became fairly level beyond one pore volume of flow and the permeability reached an equilibrium value of 2.3 x 10^{-9} cm/sec. Water was permeated through the sample for 48 days, which resulted in a total pore volume flow of 2.4.



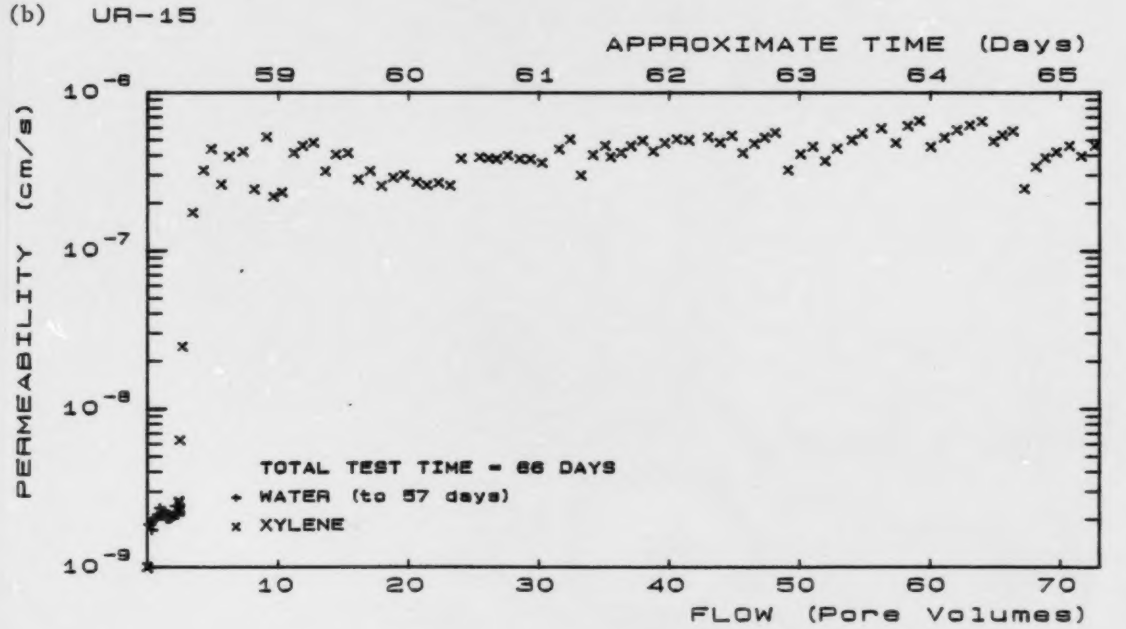


Figure 105. Permeability versus volume of flow of water and xylene through urethane grout. (a) Plot for sample UR-12. (b) Plot for sample UR-15.

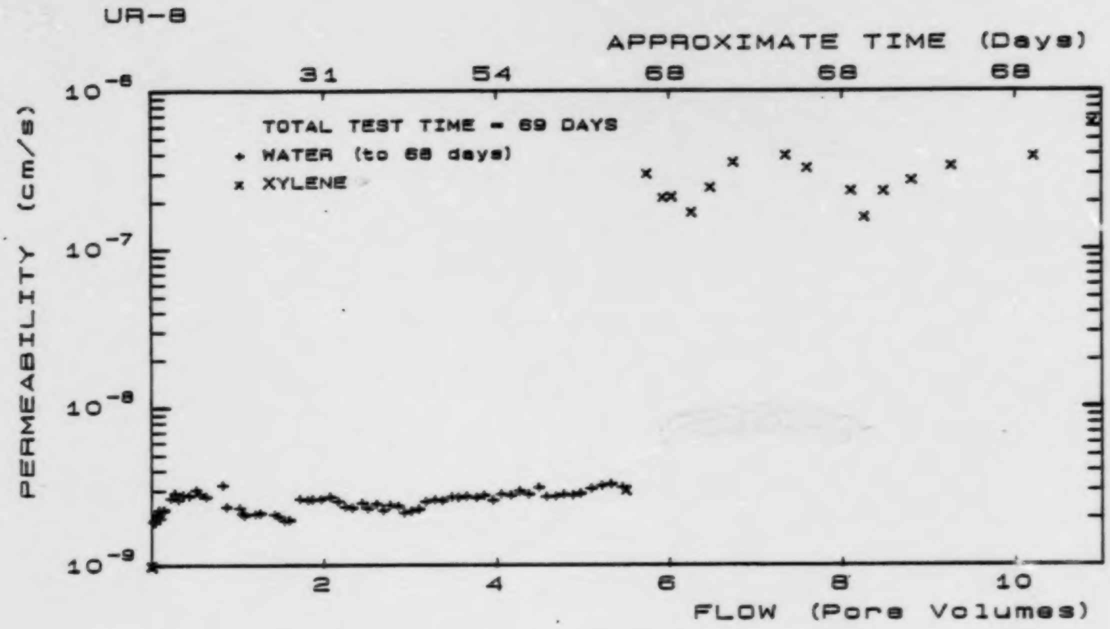


Figure 106. Permeability versus volume of flow of water and xylene through urethane grout sample UR-8.

Xylene was introduced into sample UR-12 at a headpressure of 104 kPa (15 psi), which was later increased to 138 kPa (20 psi). The tailpressure was held at zero. The net confining pressure was initially 190 kPa (27.5 psi) and was later reduced to 173 kPa (25 psi). Correspondingly, the gradient of the test was initiated at 375 and was later increased to 501. The permeability versus pore volume flow curve in Figure 105(a) shows that after the introduction of xylene, the permeability of the sample rose rapidly to a permeability plateau at 9.2 x 10^{-7} cm/sec in about 4 days of testing and with 6.6 pore volumes of xylene flow. With continued testing a second plateau was reached with a permeability of 1.2 x 10^{-6} cm/sec and 13.8 pore volumes of flow with xylene. At that point, the sample was rested without pressure. When testing was resumed, there was a slight drop in the permeability, which, with continued testing, increased and reached a third plateau with a permeability of 1.6 x 10^{-6} cm/sec, after a total xylene flow of 25.3 pore volumes. At that time the sample was again rested, and upon resumption of testing, there was a small drop again in the permeability, which was followed by a slight increase to a final equilibrium permeability of 1.24 x 10^{-6} cm/sec. This equilibrium was reached after 37 pore volumes of flow with xylene. Sample UR-12 was intermittently tested for a net period of a little over four days; however, with the rest periods during testing, the gross testing time added up to 42 days with xylene.

Xylene was introduced into sample UR-15 at a headpressure of 104 kPa (15 psi), a backpressure of zero, and a net confining pressure of 121 kPa (17.5 psi). The gradient of the test was maintained at 328. The introduction of xylene produced an immediate increase in the permeability of the sample. As shown in Figure 105(b), the sample reached its first plateau at a permeability of 4.5 x 10^{-7} cm/sec after a net flow of xylene of 2.5 pore volumes, with a net testing time of 1.75 days. With rest periods, this was spread out over a period of seven days. Upon continued testing, the permeability dropped off slightly before rising again. With intermittent testing over 21 days, the permeability of the sample reached an equilibrium of 5.2 x 10^{-7} cm/sec after a total of 38 pore volumes of flow with xylene. The intermittent testing of the sample was continued until the total xylene flow reached 70 pore volumes with little change in the permeability of the sample. This sample was on the testing line with xylene for a period of 41 days; however, it was under a hydraulic gradient for a little more than 9 days.

The authors believe that the best method of testing samples which have increases in their permeabilities of the magnitude that the above samples had, is not to continue them on the high gradient, but to gradually drop the test gradient as the permeability of the samples increases. However, equipment and space limitations required that the high headpressure, and thus the gradient, be maintained on the above samples because they shared pressure sources with other samples in the glove box.

When the two test curves on xylene are compared, it is clear that they are similar, in that the introduction of xylene caused a sharp increase in their permeabilities and both samples reached final equilibrium permeability values that were fairly close. Therefore, it can be concluded that the permeation of xylene causes from 2.5 to 3 orders of magnitude increase in the permeability of the urethane grout.

- Permeability Test of Urethane Grout With Xylene - Phase III

Two urethane grout samples, designated UR-46 and UR-47, were tested with xylene. Each sample had a thickness of 34 mm and a diameter of 75 mm. Figures 107 and 108 show the permeability versus pore volume flow graphs obtained for these samples.

Both samples were initially permeated with deionized water. Sample UR-46 was permeated with water for 18.1 days with an accumulated flow of 0.9 pore volume. Sample UR-47 was tested on water for 35.8 days with an accumulated flow of 2.7 pore volumes. The testing was conducted with a net confining pressure of 241.5 kPa (35.0 psi) for UR-46 and 120.8 kPa (17.5 psi) for UR-47, a backpressure of zero and 69.0 kPa (10 psi) for UR-46 and UR-47, respectively, and a gradient of 517 for each sample. The water permeability versus pore volume flow curves show little variation. The curve for UR-46 indicates an equilibrium permeability of 1.7 x 10^{-9} cm/sec as compared to 2.1 x 10^{-9} cm/sec for UR-47.

Reagent grade xylene was used as the chemical leachate for this pair of samples. When the chemical was introduced the net confining pressure was maintained at original levels of 241.5 and 120.8 kPa (35.0 and 17.5 psi) for UR-46 and UR-47, respectively. The backpressure was set to zero for both samples while the gradient remained at 517. Sample UR-46 was permeated with chemical for 48.2 days with an accumulated chemical flow of 18.7 pore volumes. Sample UR-47 was tested on xylene for 76.3 days with a sum chemical flow of 38.2 pore volumes. Chemical leachate/grouted soil reaction was quite similar for the two samples. Initial breakthroughs of the xylene occurred after approximately 24 hours and a flow of less than 0.3 pore volume. The initial permeability plateaus agreed with the final equilibrium permeabilities rather well. Final equilibrium permeability of sample UR-46 was 4.5 x 10^{-7} cm/sec, contrasted to 1.4 x 10^{-6} cm/sec for UR-47, a nearly threefold variation. It is important to note that these final equilibrium permeabilities were inversely proportional to the net confining pressures on the samples. Due to the increased permeabilities, the permeation of the samples had to be performed periodically with varying rests periods, generally one to five days, in between.

Small amounts of gas began to percolate through the effluent lines after the establishment of the initial permeability plateau. Gas production increased to a maximum output of one bubble per five seconds from the 3.2 mm (0.125 in.) nylon flexible tubing into the effluent standpipe. The amount eventually leveled off to approximately one bubble per fifteen seconds which continued throughout the permeation process. UR-46 had a total of six percolation periods spanning seven days, while UR-47 had a total of five percolation cycles over a period of eight days.

After reaching equilibrium, the gradients were reduced five-fold to a new level of 104. The net confining pressures were unchanged at 241.5 kPa (35.0 psi) for UR-46 and 120.8 kPa (17.5 psi) for UR-47. Backpressures were maintained at zero. Both samples exhibited a remarkable reduction in permeability, too low to be measured due to the decrease in gradient. For the sake of graphical presentation a value of 1.0 x 10^{-12} cm/sec was assigned to

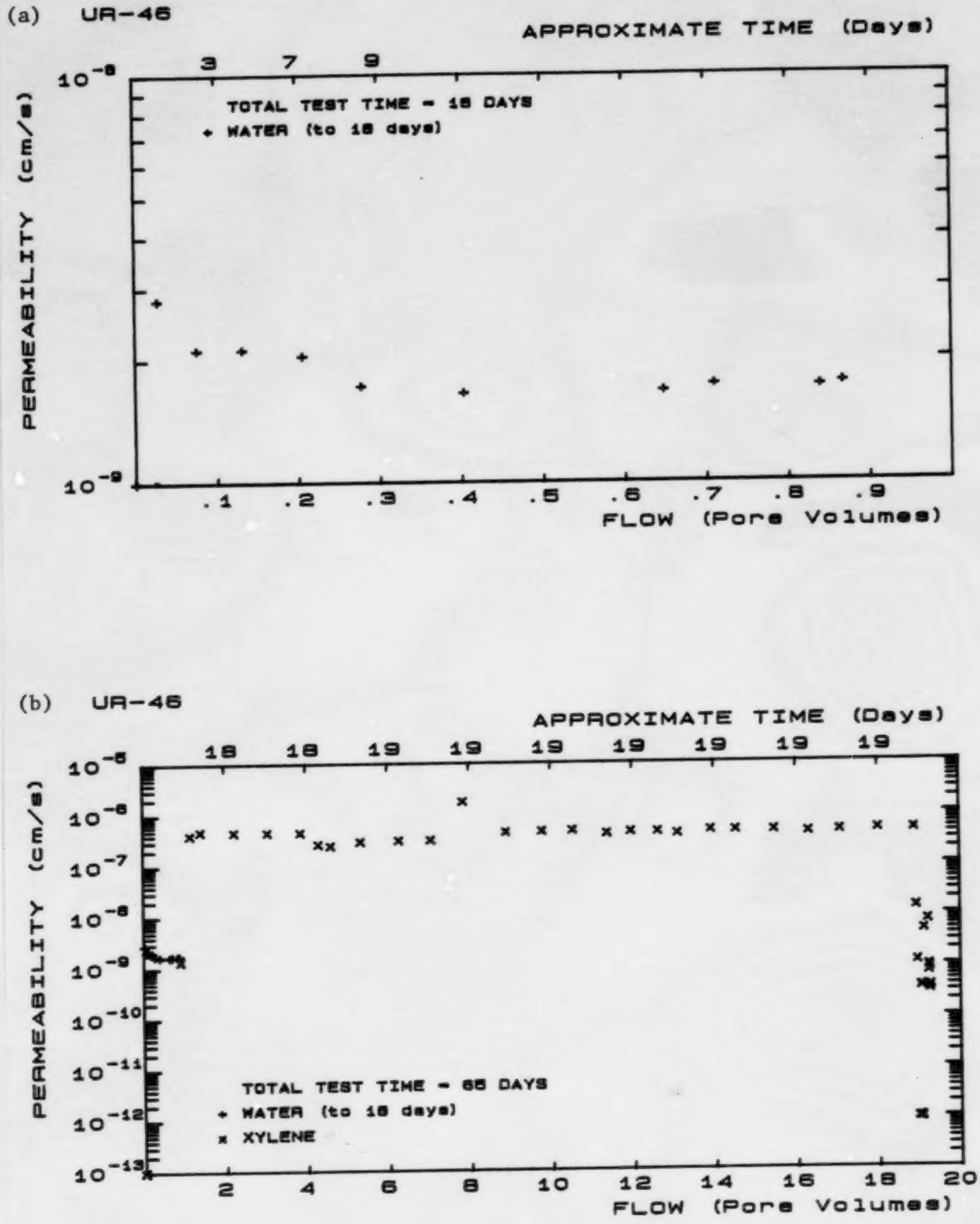
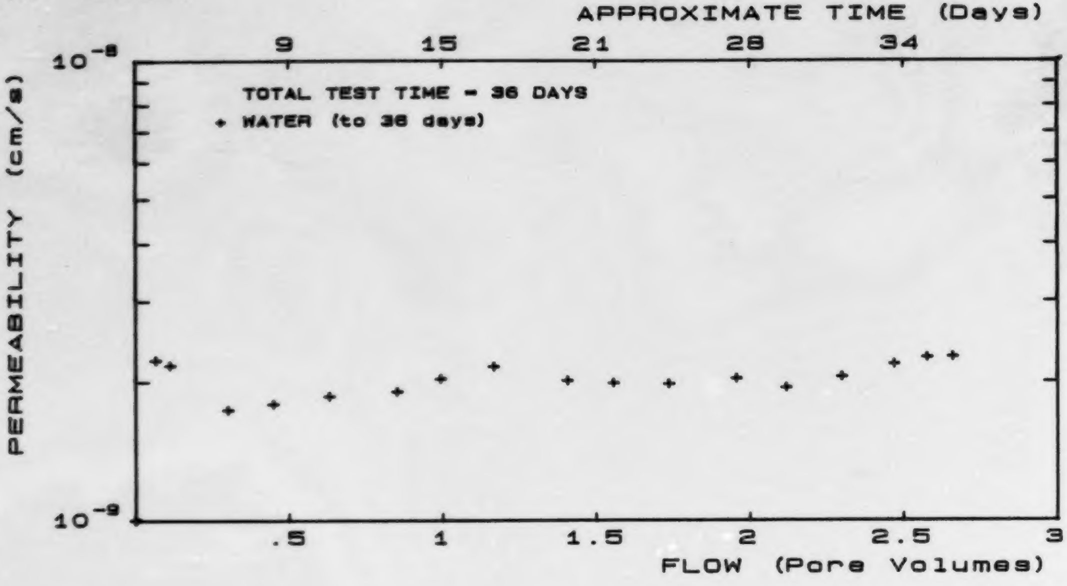


Figure 107. Permeability versus volume of flow through urethane grout sample UR-46. (a) Water as permeant. (b) Water and xylene as permeants.

(a) UR-47



(b) UR-47

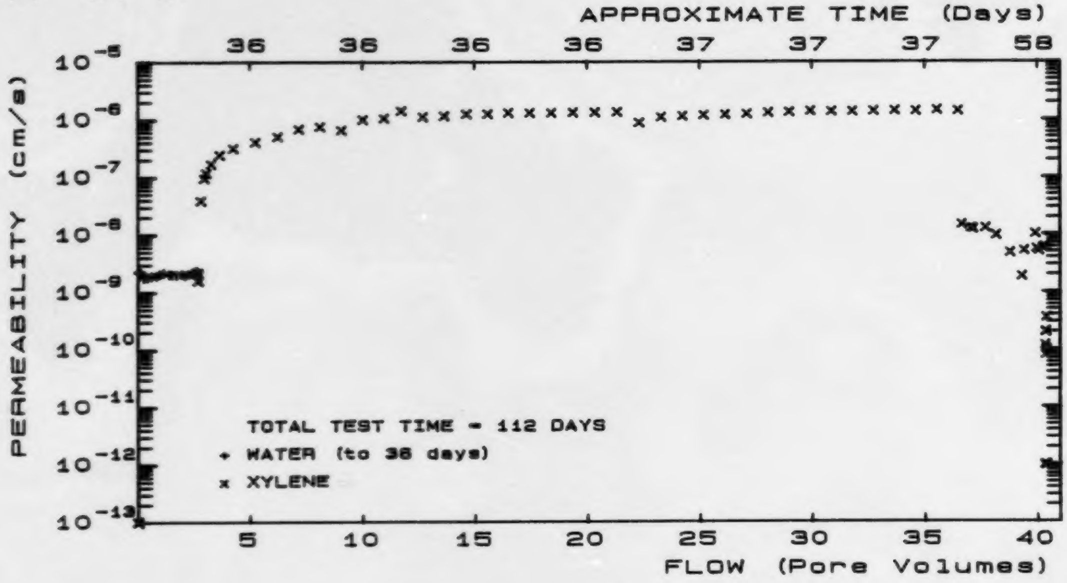


Figure 108. Permeability versus volume of flow through urethane grout sample UR-47. (a) Water as permeant. (b) Water and xylene as permeants.

this particular condition. The permeability of sample UR-46 dropped rapidly to 1.0×10^{-12} cm/sec and remained at that level for nearly twenty-one days, after which the permeability oscillated in the range of 3.1×10^{-10} cm/sec to 7.4×10^{-9} cm/sec. The average of these values calculates to be 1.7×10^{-9} cm/sec, almost identical to the water baseline permeability of the sample.

The permeability of sample UR-47 did not drop off completely at first. Thirty days and four pore volumes later the permeability of the sample could not be measured, thus was assigned a permeability of 1.0×10^{-12} cm/sec. Intermittently, flow could be measured yielding permeabilities in the range of 1.0×10^{-10} cm/sec. Prior to the period of immeasurable flow the average permeability was 2.4×10^{-9} cm/sec, which was almost equal to its water baseline permeability.

- Analysis of Permeability Test Results For Urethane Grout

Figure 109 illustrates the overall changes in permeability of urethane grout with ten selected chemicals. The summary is given in a bar chart form (see section entitled Analysis of Permeability Test Results For Acrylate Grout for the interpretation of this chart).

As shown the urethane grout remained quite impervious with the majority of the chemicals. With 20% cupric sulfate and 4N hydrochloric acid the grout performed marginally, as its final permeabilities slightly exceeded the 1×10^{-7} cm/sec level. The most detrimental to the urethane grout were the 25% sodium hydroxide and xylene. The sodium hydroxide caused a 4.5 orders of magnitude increase in the permeability of the urethane grout, while with xylene the permeability of the grout increased by 2.5 orders of magnitude.

The different concentrations of the chemicals had varying effects on the urethane grout. To illustrate this, Figures 110 through 112 show test plots for urethane grout samples with three different chemicals, each plot with two concentrations of the selected chemical.

Figure 110 shows the changes in the permeability of urethane grout with a 100% and 25% solution of ethylene glycol, respectively. As can be seen, with 25% ethylene glycol the urethane grout samples did not exhibit an increase in permeability, while the samples with 100% solution of ethylene glycol did. This happened even though the gradient was higher for the 25% ethylene glycol tests.

Figures 111 and 112 illustrate the cases where the concentration of neither the hydrochloric acid nor the sodium hydroxide made any measurable difference in the rate or magnitude of changes in the permeability of the urethane grout.

Overall Comparison of the Effectiveness of Grouts as Barriers

- Effectiveness of Grouts With Water

The average equilibrium permeability of the grouts tested with water

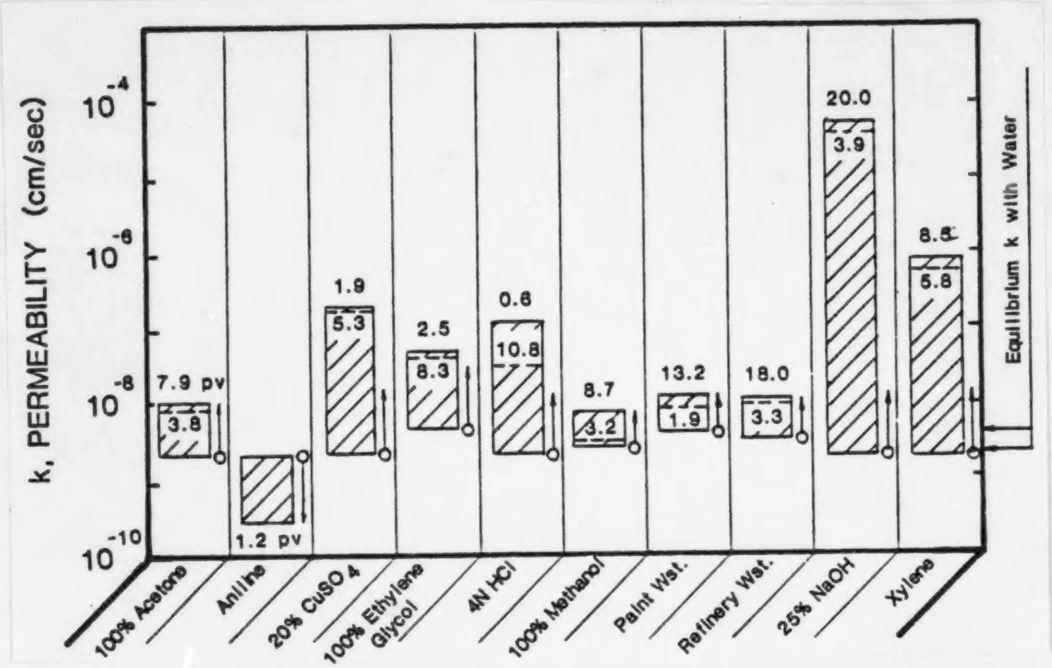


Figure 109. Permeability of urethane grout with various chemicals.

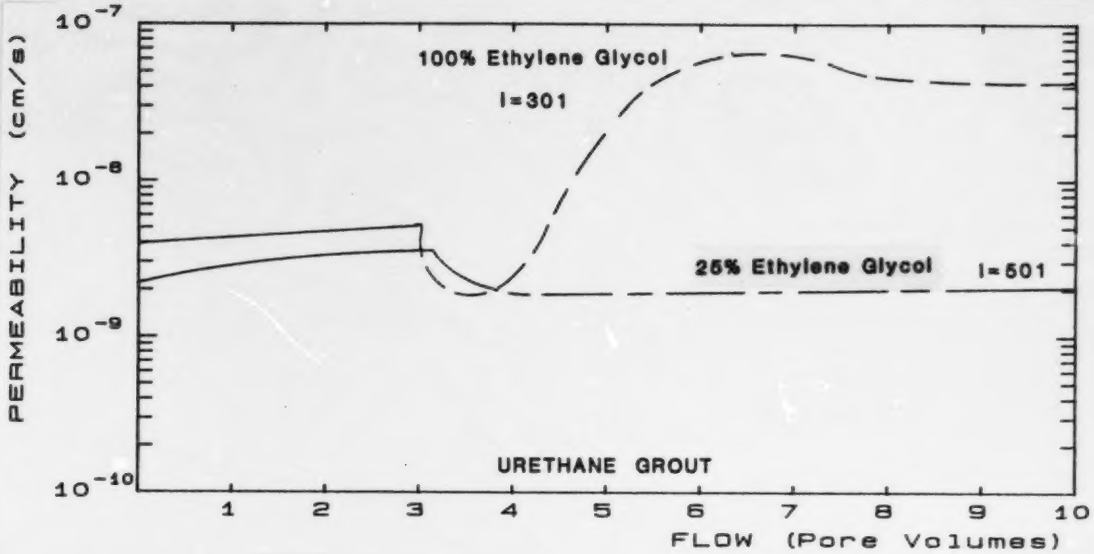


Figure 110. Permeability of urethane grout with 100% and 25% ethylene glycol.

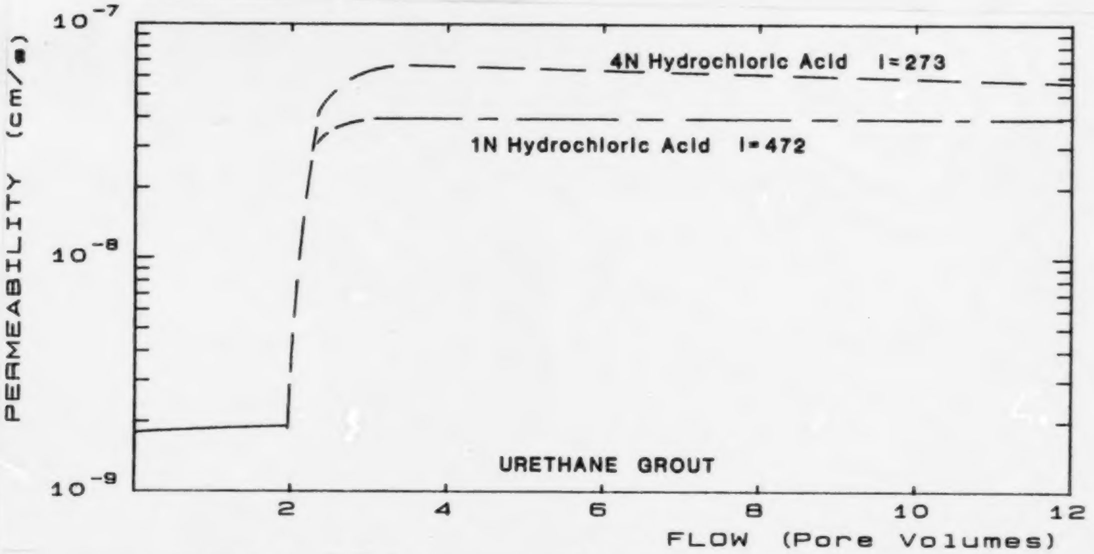


Figure 111. Permeability of urethane grout with 1N and 4N hydrochloric acid.

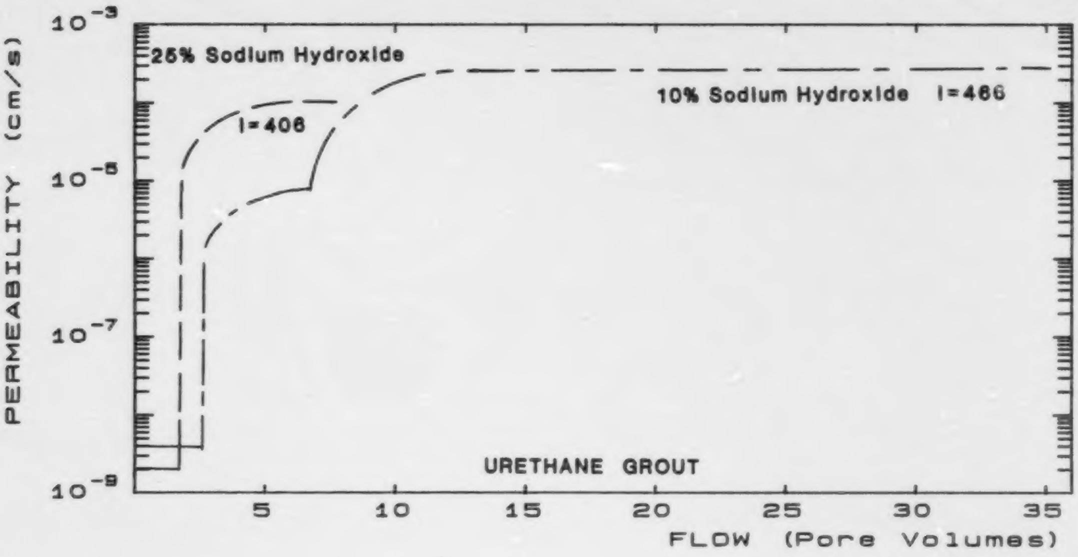


Figure 112. Permeability of urethane grout with 25% and 10% sodium hydroxide.

ranged from a low of 2.3 x 10^{-10} cm/sec to a high of 5 x 10^{-5} cm/sec. Table 12 shows the equilibrium permeabilities of the various grouts with water.

From the point of view of impervious cutoff construction, the permeability of a grouted soil should not exceed 1 x 10^{-7} cm/sec. It can be seen that the equilibrium permeabilities of the acrylate, cement-bentonite (mix 2) and urethane grouts with water stayed much below the 1 x 10^{-7} cm/sec value. On the other hand, the permeabilities of the other four grouts exceeded it.

- Effectiveness of the Grouts With Acetone

Figure 113 shows the effects of the 100% solution of acetone on the acrylate, urethane, cement-bentonite (mix 1), cement-bentonite (mix 2) and sodium silicate grouts, and the effect of the 25% solution of acetone on acrylate grout.

As shown, the 100% acetone affected the acrylate grout the most, causing an increase of 5.5 orders of magnitude in its permeability. It had a moderate effect on the permeability of the cement-bentonite (mix 1) grout, and minor to negligible effects on the permeabilities of the urethane, sodium silicate and cement-bentonite (mix 2) grouts. In fact, the permeability of the cement-bentonite (mix 2) grout decreased with the permeation of the 100% solution of acetone.

It is also shown in Figure 113 that the permeation of a 25% acetone solution caused a moderately high (approximately 1.75 orders of magnitude) increase in the permeability of the acrylate grout, which is considerably smaller than what the grout experienced with the 100% solution of acetone.

In grouted cutoff construction it is suggested that the permeability of the grouted soil not rise above 1 x 10^{-7} cm/sec. The final equilibrium permeability of the following grouts with a 100% solution of acetone did not exceed 1 x 10^{-7} cm/sec: urethane and cement-bentonite (mix 2). With the 25% solution the permeability of the acrylate also stayed below the 1 x 10^{-7} cm/sec threshold permeability value.

- Effectiveness of the Grouts With Aniline

Figure 114 shows the effects the reagent grade aniline had on the acrylate, urethane and cement-bentonite (mix 2) grouts.

As can be seen, the reagent grade aniline had a substantial effect on the acrylate grout, increasing its permeability by 4 orders of magnitude. In contrast, the permeation of aniline through the urethane and cement-bentonite (mix 2) grouts resulted in decreases in the permeabilities of these grouts by as much as 0.8 to 0.9 order of magnitude.

From the standpoint of cutoff construction, the permeability of a grouted soil should not exceed 1 x 10^{-7} cm/sec, even after the permeation of chemicals. The permeation of reagent grade aniline caused the permeability of the acrylate grout to rise above the 1 x 10^{-7} cm/sec level, while the final equilibrium

TABLE 12. SUMMARY OF THE EQUILIBRIUM PERMEABILITIES OF THE VARIOUS GROUTS WITH WATER

GROUT	EQUILIBRIUM PERMEABILITIES (cm/sec)
acrylate	5.1×10^{-10}
cement-bentonite (mix 1)	3.0×10^{-6}
cement-bentonite (mix 2)	2.3×10^{-10}
sodium silicate	5.0×10^{-5}
glyoxal-modified sodium silicate	1.9×10^{-5}
sodium aluminate-modified sodium silicate	1.7×10^{-5}
urethane	3.6×10^{-9}

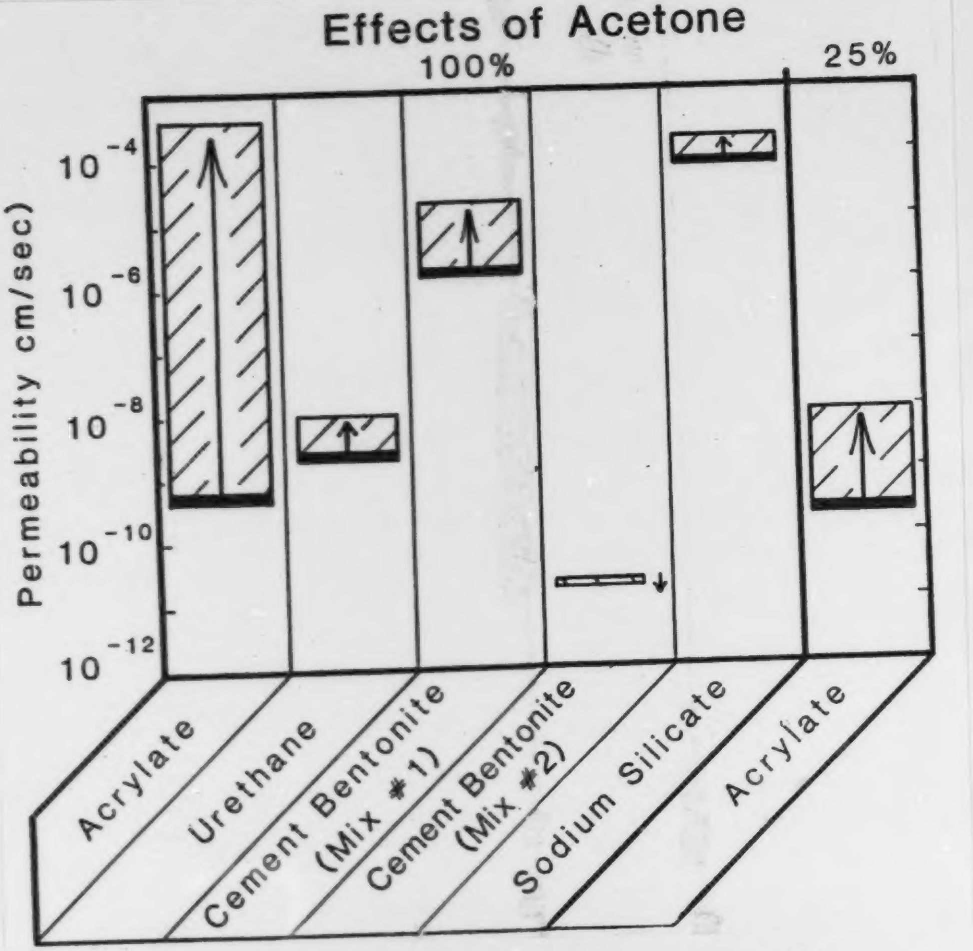


Figure 113. Effects of acetone on the permeability of various grouts.

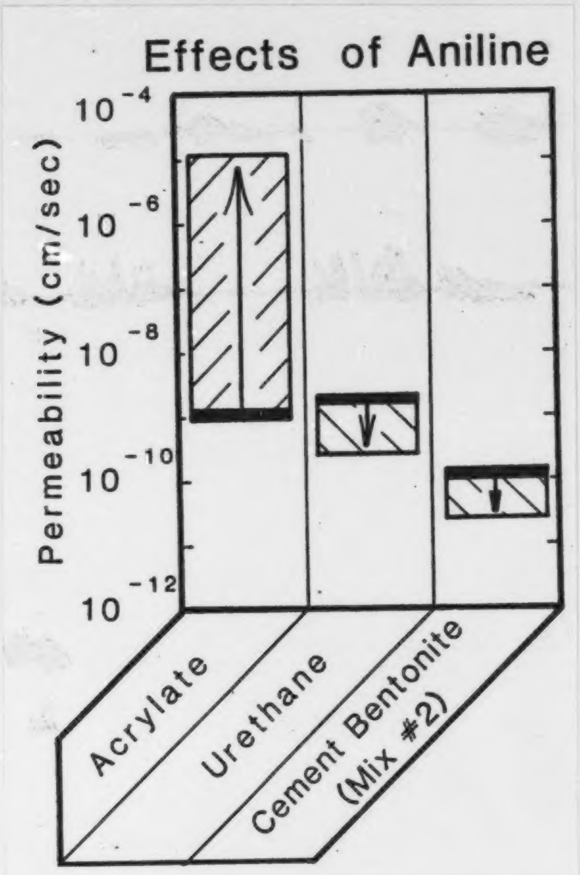


Figure 114. Effects of aniline on the permeability of various grouts.

permeabilities of the urethane and cement-bentonite (mix 2) grouts were much below this limit.

- Effectiveness of the Grouts With Cupric Sulfate

Figure 115 shows the effects of a 20% solution of cupric sulfate on acrylate, urethane, cement-bentonite (mix 2), glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate grouts, and the effect of a 10% solution of cupric sulfate on the acrylate grout.

As may be observed, cupric sulfate of both concentrations had strong effects on the acrylate grout, increasing its permeability by nearly 3 orders of magnitude. The percolation of a 20% solution of cupric sulfate also increased the permeability of the urethane samples by 2 orders of magnitude. On the other hand, the permeability of the cement-bentonite (mix 2) grout was reduced by a little more than 1 order of magnitude by the permeation of the cupric sulfate. With cupric sulfate flow the permeability of both sodium silicate grouts tested was reduced by 0.5 to 0.33 order of magnitude.

The glyoxal-modified sodium silicate and the sodium aluminate-modified sodium silicate grouts had permeabilities which even with water exceeded 1×10^{-7} cm/sec, the limit value for cutoff construction. The average final permeability of the urethane grout with the 20% solution of cupric sulfate was 2.1×10^{-7} cm/sec, barely exceeding the 1×10^{-7} cm/sec limit. Even though the permeability of the acrylate grout samples increased by 3 orders of magnitude with both solutions of cupric sulfate, their final equilibrium permeabilities were still below 1×10^{-7} cm/sec.

- Effectiveness of the Grouts With Ethylene Glycol

The effects of ethylene glycol on four types of grouts are shown in Figure 116. The grouts tested with reagent grade ethylene glycol were acrylate, urethane, cement-bentonite (mix 1), and sodium silicate. The urethane grout was also tested with a 25% solution of ethylene glycol.

The permeation of the reagent grade ethylene glycol caused a little more than a 2 orders of magnitude increase in the permeability of the acrylate grout samples, and approximately a 1 order of magnitude increase in the permeability of the urethane grout samples. On the other hand, the permeabilities of both the cement-bentonite (mix 1) and the sodium silicate grouts were reduced by more than 1 order of magnitude. The percolation of the 25% solution of ethylene glycol through the urethane samples caused their average permeability to decrease slightly.

With respect to cutoff structure construction, where a limiting maximum permeability of 1×10^{-7} cm/sec may be used, both the acrylate and urethane grouts performed well with ethylene glycol, their ultimate equilibrium permeabilities lying below the limit permeability. Neither the cement-bentonite (mix 1) grout, nor the sodium silicate grout would be recommended for cutoff applications, as their baseline permeabilities were much above the 1×10^{-7} cm/sec limit.

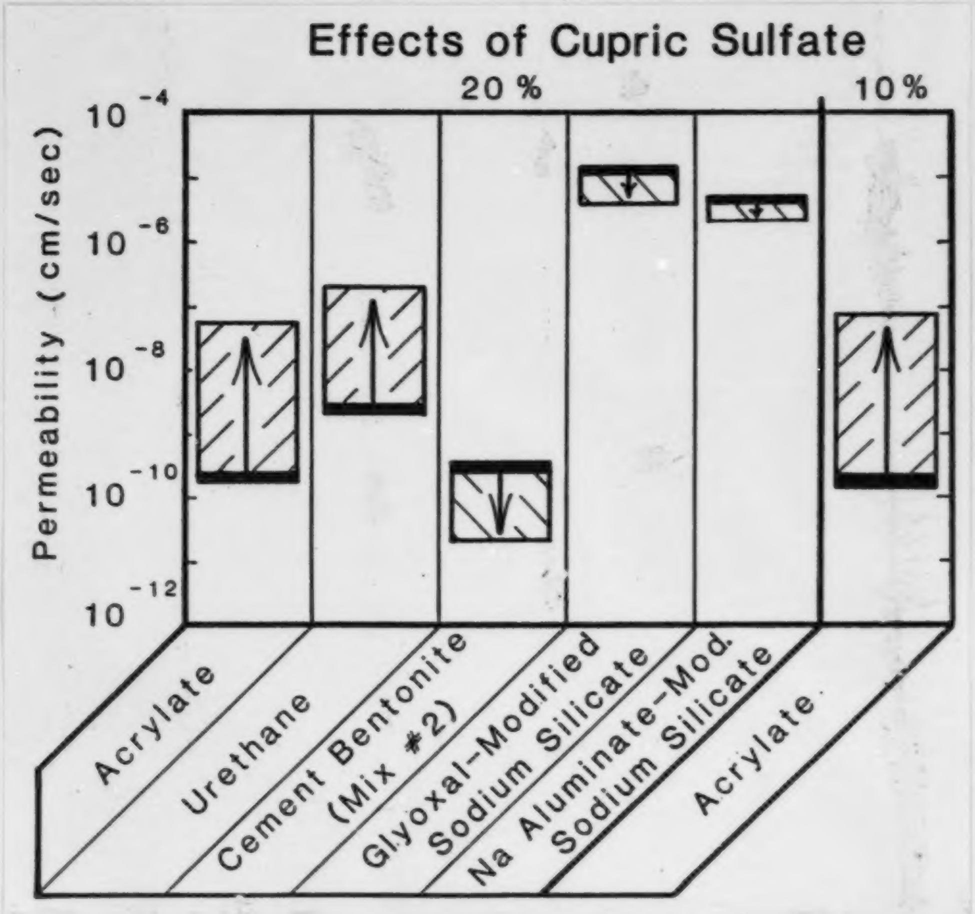


Figure 115. Effects of cupric sulfate on the permeability of various grouts.

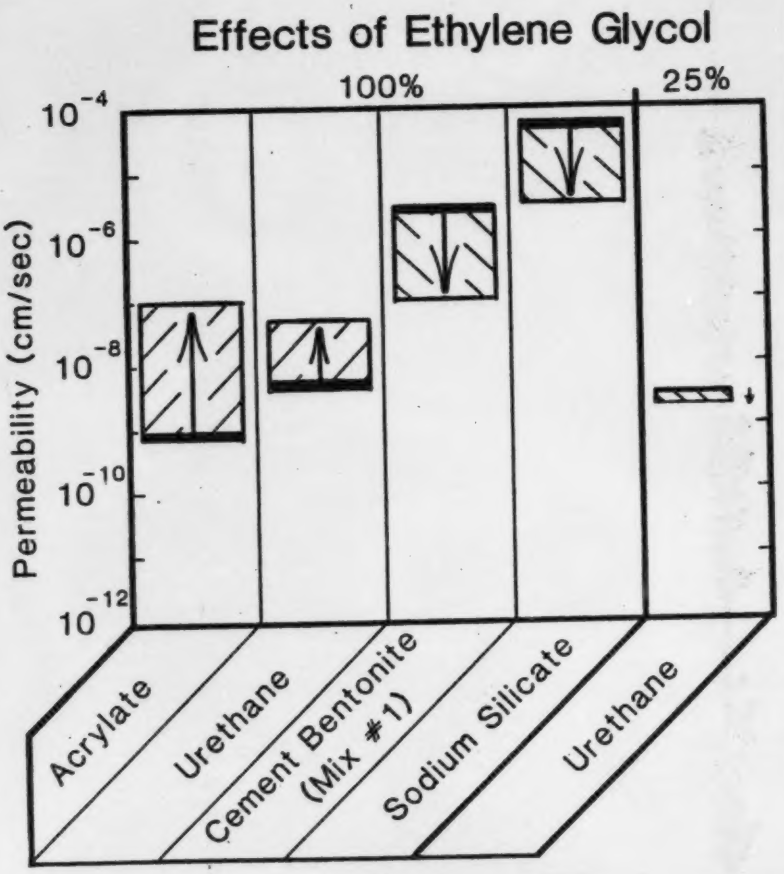


Figure 116. Effects of ethylene glycol on the permeability of various grouts.

- Effectiveness of the Grouts With Hydrochloric Acid

Acrylate, urethane, and cement-bentonite (mix 2) grouts were tested with a 4N solution of hydrochloric acid. The acrylate and urethane grouts were also tested with a 1N solution of hydrochloric acid. Figure 117 shows the results of these tests.

As can be seen, the acrylate grout reacted sharply to the permeation of both concentrations of hydrochloric acid, causing an approximately 4 orders of magnitude increase in the permeability of the samples. The leaching of both solutions of hydrochloric acid increased the permeability of the urethane grout samples by a little more than 1 order of magnitude. The permeation of the 4N solution of hydrochloric acid caused a nearly 1 order of magnitude decrease in the already low permeability of the cement-bentonite (mix 2) grout.

From the standpoint of cutoff construction, the permeability of a proposed grout may not be greater than 1 x 10^{-7} cm/sec, either with water or with any of the chemicals. With either of the hydrochloric acid concentrations that were investigated, the final equilibrium permeability of the acrylate grout exceeded the above limit by a considerable margin. On the other hand, both the urethane and cement-bentonite (mix 2) grouts had final equilibrium permeabilities that stayed under the 1 x 10^{-7} cm/sec limit.

- Effectiveness of the Grouts With Methanol

Figure 118 shows the effects of reagent grade methanol on acrylate, urethane, cement-bentonite (mix 1), and cement-bentonite (mix 2) grouts, and the effect of a 25% solution of methanol on acrylate grout.

As illustrated, the reagent grade methanol had a very pronounced effect on the acrylate grout, causing an increase of approximately 5.5 orders of magnitude in its permeability. It induced only a 0.5 order of magnitude increase in the permeability of the urethane grout, and caused minor reductions in the permeabilities of the two types of cement-bentonite grout samples.

The permeation of the 25% solution of methanol caused only a moderate 1 order of magnitude increase in the permeability of the acrylate grout samples, a much smaller increase than what the reagent grade concentration of methanol caused.

Using an upper limit permeability of 1 x 10^{-7} cm/sec for grouts to be used in cutoff construction, it is seen that the permeation of reagent grade methanol caused the permeability of the acrylate grout to exceed this limit by a large margin, and that the permeability of the cement-bentonite (mix 1) grout exceeds that limit even with water. In contrast, the final permeabilities of the urethane and cement-bentonite (mix 2) grouts with reagent grade methanol, and the acrylate grout with the 25% solution of methanol, stayed much below the above limit.

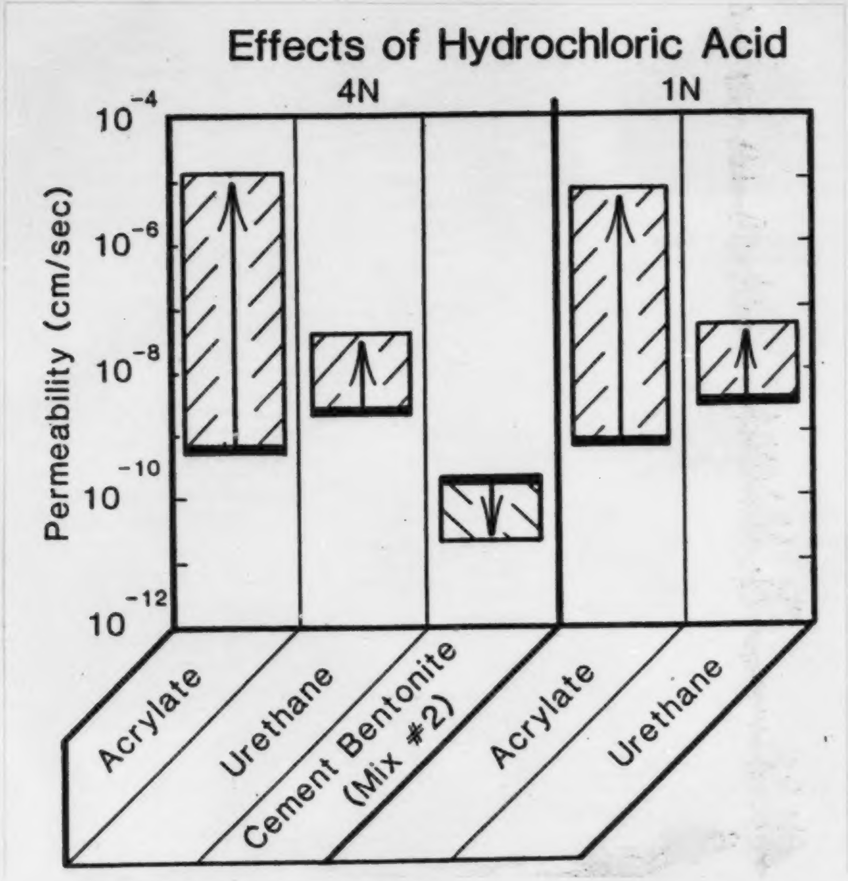


Figure 117. Effects of hydrochloric acid on the permeability of various grouts.

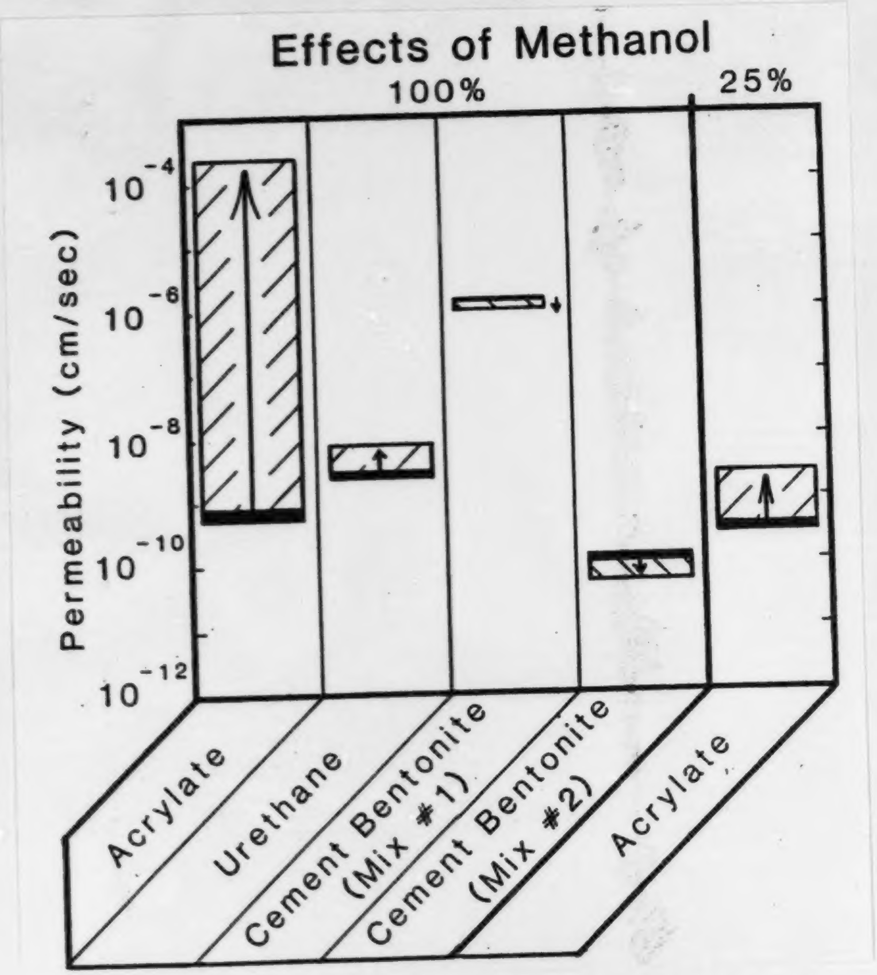


Figure 118. Effects of methanol on the permeability of various grouts.

- Effectiveness of the Grouts With Real-Site Paint Waste

The effects of real-site paint waste on four types of grouts are shown in Figure 119. The grouts tested with paint waste included acrylate, urethane, cement-bentonite (mix 1), and sodium silicate.

The permeation of paint waste had relatively limited effect on the grouts tested. It caused an approximately 0.5 order of magnitude increase in the permeability of both the acrylate and urethane grouts. It caused a 0.5 order of magnitude decrease in the permeability of the cement-bentonite (mix 1) grout, which may have been due to the growth and deposition of microorganisms in the voids of the grouted soil samples. The percolation of paint waste resulted in a very small decrease in the permeability of the sodium silicate grout samples.

Using the permeability of 1 x 10^{-7} cm/sec as an upper threshold value for grouts to be used in barrier construction, both the acrylate and urethane grout samples had final permeabilities with paint waste which were much below this limit. However, both the cement-bentonite (mix 1) and the sodium silicate grouts had permeabilities that were above the threshold value even with water.

- Effectiveness of the Grouts With Real-Site Refinery Waste

The permeabilities of acrylate, urethane, cement-bentonite (mix 1), and sodium silicate grout samples were tested with real-site refinery waste.

In general, as shown in Figure 120, the refinery waste had little detrimental effect on these grouts. It caused approximately a 0.5 order of magnitude increase in the permeability of both the acrylate and urethane grouts, while the permeabilities of both the cement-bentonite (mix 1) and the sodium silicate grouts decreased. These reductions in permeability were more than 1.5 orders of magnitude and may have been caused by microorganisms blocking the flowpaths in the samples.

The final permeabilities of both the acrylate and urethane grouts were below 1 x 10^{-7} cm/sec, thus they could be used as barriers to contain this particular refinery waste. The cases of the cement-bentonite (mix 1) and sodium silicate grouts are interesting. Both had baseline permeabilities with water that were above 1 x 10^{-6} cm/sec, however, with refinery waste their final permeabilities ended up near or below the 1 x 10^{-7} cm/sec threshold value.

- Effectiveness of the Grouts With Sodium Hydroxide

Figure 121 shows the effects of a 25% solution of sodium hydroxide on acrylate, urethane, cement-bentonite (mix 2), glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate grouts, and the effect of a 10% solution of sodium hydroxide on the urethane grout.

As can be seen, the 25% solution of sodium hydroxide had varied effects on the above grouts. Its permeation through the urethane grout resulted in a 3.75 orders of magnitude increase in the permeability of the grout. On the

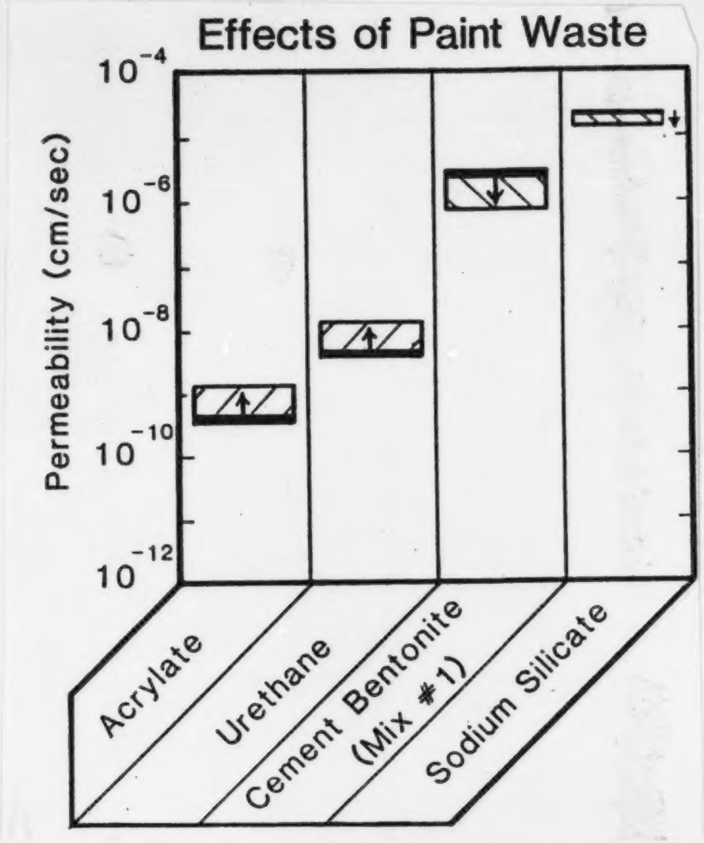


Figure 119. Effects of real-site paint waste on the permeability of various grouts.

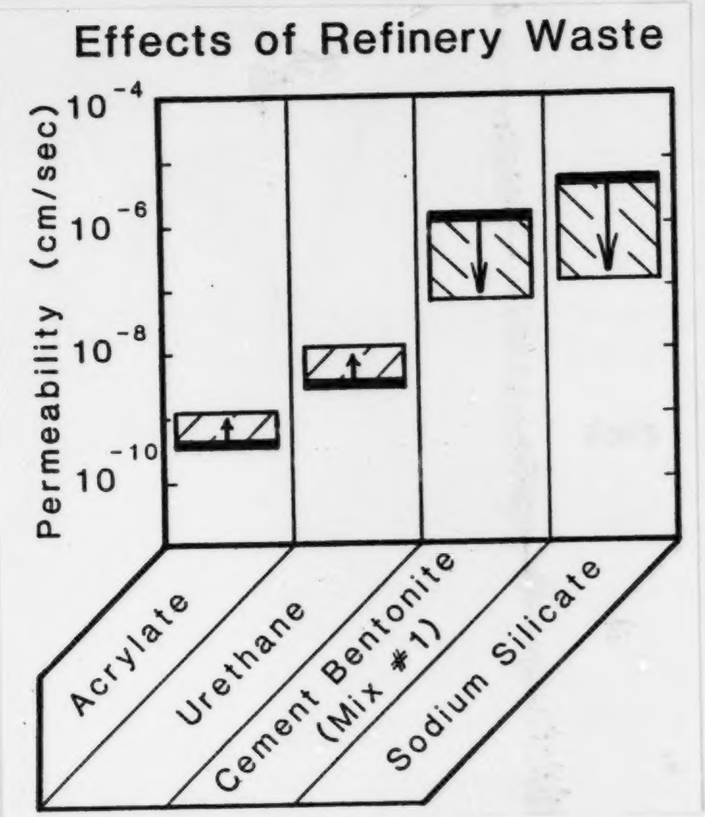


Figure 120. Effects of real-site refinery waste on the permeability of various grouts.

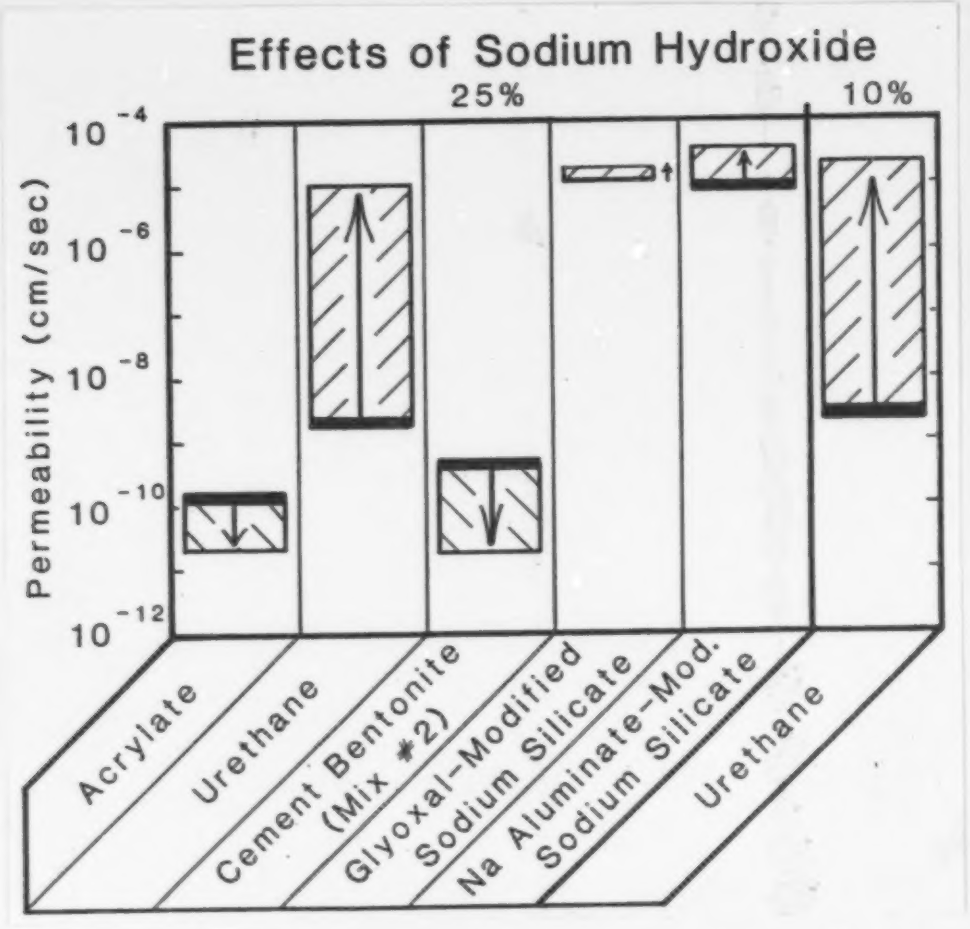


Figure 121. Effects of sodium hydroxide on the permeability of various grouts.

other hand, the chemical caused a 1 order of magnitude decrease in the permeability of the acrylate grout, a 1.5 orders of magnitude decrease in the permeability of the cement-bentonite (mix 2) grout, and minor increases in the permeabilities of the two types of sodium silicate grouts.

The permeation of the 10% solution of sodium hydroxide through the urethane grout caused a 4 orders of magnitude increase in the permeability of the grouted samples, practically the same effect as the permeation of the 25% solution.

The acrylate and cement-bentonite (mix 2) grouts behaved well with sodium hydroxide, their permeabilities staying much under the limiting value of 1 x 10^{-7} cm/sec. In contrast, the final permeability of the urethane grout samples rose above the 1 x 10^{-7} cm/sec limit with both concentrations of the chemical. The permeabilities of the two sodium silicate grouts were approximately 1 x 10^{-5} cm/sec with water alone, too high for considering these grouts for cutoff construction.

- Effectiveness of the Grouts With Xylene

The effects of reagent grade xylene on six types of grouts are shown in Figure 122. The grouts tested with xylene included acrylate, urethane, cement-bentonite (mix 1), sodium silicate, glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate.

The permeation of reagent grade xylene caused a 2.5 orders of magnitude increase in the permeabilities of both the acrylate and urethane grouts, and a 0.5 order of magnitude increase in the permeability of the glyoxal-modified sodium silicate grout. In contrast, the other three grouts underwent reductions in their permeabilities. The sodium aluminate-modified sodium silicate grout showed a decrease of 3.5 orders of magnitude, the cement-bentonite (mix 1) grout underwent a 1.75 orders of magnitude reduction, while the sodium silicate grout experienced a 0.75 order of magnitude reduction in their permeabilities.

With respect to hazardous waste barrier construction, where a limiting maximum permeability of 1 x 10^{-7} cm/sec may be used, only the acrylate grout performed satisfactorily. Its final permeability with xylene rose just to the above limit. For each of the other five grouts, either their final permeability with xylene, or their baseline permeability with water, exceeded the 1 x 10^{-7} cm/sec limit.

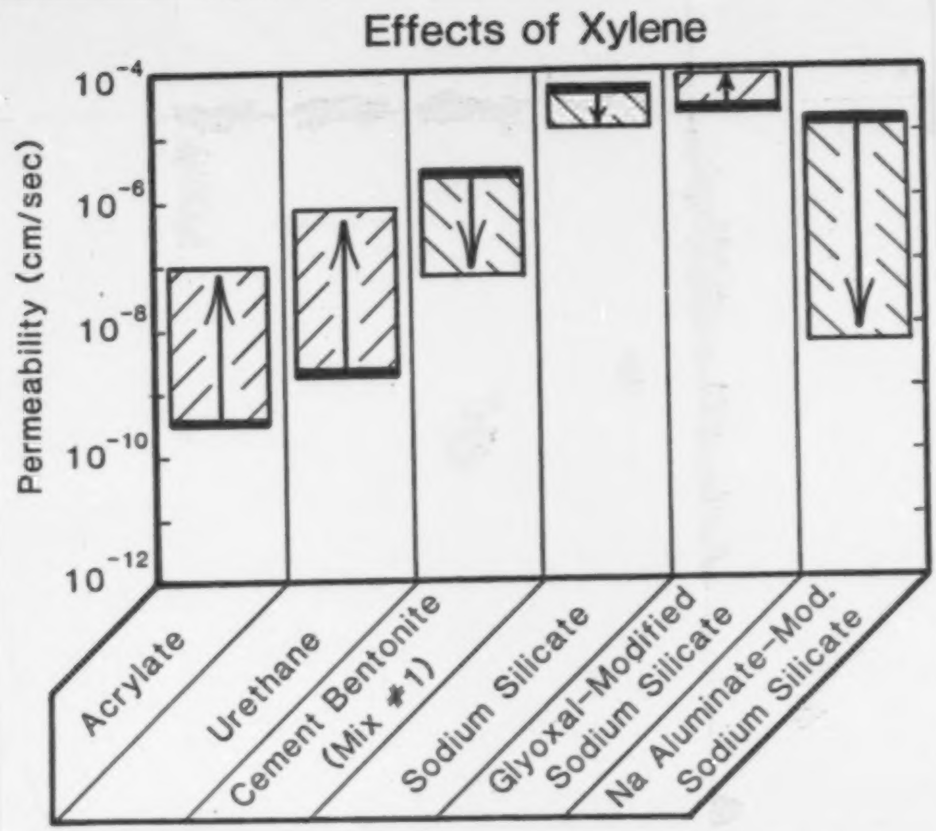


Figure 122. Effects of xylene on the permeability of various grouts.

REACTIVITY TESTS

The preparation of reactivity samples is outlined in Section 4 of this report. As described there, three replicate grout samples were prepared for each grout-chemical combination. Each sample was cylindrical in shape, 25 mm in both diameter and thickness. ASTM Standard C127-82 "Standard Test Method for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings" was followed for the preparation, immersion and weighing of the specimens. After the required curing period, the samples were immersed in selected chemicals in labeled beakers for 84 days. The beakers were sealed to reduce evaporation. Weight measurements were made on the samples at time intervals of 1, 7, 14, 28, 56, and 84 days. Plots of percent weight change versus time were prepared for each sample and replicate series.

When a grouted sample is exposed to a chemical, a reaction may develop between them and the sample may increase or decrease in weight, or remain unchanged. The weight loss may be due to water loss (shrinkage) or spalling. In addition, the grout samples may become hard or soft, or may even become soft and sticky (glue-like).

The maximum average weight gain among the grouts tested in this project was 45% for the urethane grout with aniline. The maximum weight loss was 23% for the cement-bentonite (mix 1) grout with acetone. Cement-bentonite (mix 2) grout immersed in 4N hydrochloric acid underwent almost total disintegration as did urethane grout immersed in 25% sodium hydroxide.

Based on the range of percent weight changes found in the whole test series, the following qualitative terms have been chosen to describe the relative weight changes of specific grouts:

Percent weight change:	0-5	5-10	10-15	15-20	20-25	above 25
Qualitative description of reaction:	low	medium low	medium	medium high	high	very high

The four different grouts tested for their reactivity were acrylate, cement-bentonite (mix 1), cement-bentonite (mix 2), and urethane. Reactivity tests were not conducted on the sodium silicate, glyoxal-modified sodium silicate and the sodium aluminate-modified sodium silicate grout samples because these grouts had high permeabilities even with water and were deemed unsuitable for barrier construction.

Reactivity Tests of Acrylate Grout

The standard 25 mm diameter by 25 mm thick cylindrical acrylate grout samples were prepared by first compacting sand into the molds, then injecting the acrylate grout into the sand using a hypodermic needle. The grouted samples were left to set, then removed from their molds, and cured in a moist room. The samples were grayish white in color and felt like hard rubber once cured. After they had been weighed and measured, three replicates were immersed in water, and into each of the following chemicals: 100% acetone, aniline, 20% cupric sulfate, 100% ethylene glycol, 4N hydrochloric acid, 100% methanol, real-site paint waste, real-site refinery waste, 25% sodium hydroxide, and xylene.

The acrylate grout samples underwent a maximum gain in weight of 20.3% in water after just one day of immersion, and suffered a maximum weight loss of 20% in real-site refinery waste over a period of 56 days.

The following sections describe the reactivity of acrylate grout samples with water and various chemicals.

- Reactivity Test of Acrylate Grout With Deionized Water

Three acrylate samples were tested for their reactivity with water. All three samples were cylindrical in shape and were 25 mm in both diameter and thickness.

The three samples were immersed in deionized water for only 7 days. After one day of testing the samples gained an average of 20.3% of their initial weight and became jelly-like in consistency. By the 7th day, the samples softened to the point that they lost their shape and could not be weighed.

All three samples behaved essentially the same, the first day percent weight changes being gains of 17.9, 28.2, and 14.9%, and all three samples lost their shape by the 7th day. The level of swelling of the acrylate samples with water is considered to be medium high to high.

- Reactivity Test of Acrylate Grout With 100% Acetone

The reactivity of three acrylate samples was tested with 100% acetone. The samples were cylindrical and of the standard size of 25 mm in diameter and 25 mm in thickness.

The samples were immersed in 100% acetone for 84 days. Their weights were measured at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. Figure 123 shows the percent of weight change versus time plots that resulted from the testing of the three samples. As can be seen, the samples lost an average of 4.5% of their initial weight by the end of the first day and then continued to lose more weight until the 7th day, by which time they lost an average of 6.3% of their initial weight. Thus, the bulk of the weight loss occurred in the early days of testing. Continued testing resulted in some slight fluctuations in the test curves. The ultimate, or 84 day magnitude of weight loss, was 7.1%, or not much different from the 7th-day value.

The consistency of the samples over the test period changed as follows. After only one day of testing, as the samples lost weight, they also became hard. By the 7th day, they were very hard. On the 28th day, the samples were still very hard, but by then, their surfaces became coarse, sandy and showed signs of flaking.

- Reactivity Test of Acrylate Grout With Aniline

Three acrylate samples were tested for their reactivity to aniline. The samples were cylindrical and had the standard dimensions of 25 mm in both diameter and thickness. Figure 124 shows the percent weight change versus time plots that were obtained from the testing of the samples by immersion in aniline for 84 days.

As shown in the figure, the three samples underwent relatively small weight changes. It is noted that one of the samples lost 1.6% of its weight during the first day of testing, while the other two lost less than 0.2%. This discrepancy is considered negligible. Also, after the first day, the shapes of the three test plots are very similar.

Based on averaging the results from the three samples, 0.5% of their weight was lost during the first day, and no change was exhibited between the first and 7th days. After the 7th day the samples began to gain weight. Their average weight loss was reduced to 0 by the 28th day, and they reached an average of 0.4% weight gain by the 56th day. The average weight gain dropped to 0.1% by the 84th day.

The initially hard rubber-like consistency of the samples became hard by the 28th day and remained so until the end of the tests. The initially grayish-white color of the samples turned brown by the 56th day and remained that way through the rest of the testing period.

As observed, the three samples behaved quite consistently with respect to weight changes with elapsed time. One sample had a small initial offset at the beginning of the testing and this offset persisted throughout the test period. However, the shape of the plots showed remarkable consistency beyond the first day. Overall, the three samples underwent low levels of weight changes during 84 days of testing with aniline.

- Reactivity Test of Acrylate Grout With 20% Cupric Sulfate

Three acrylate samples were tested for their reactivity to 20% cupric sulfate. Each cylindrical sample had the standard size of 25 mm in both diameter and thickness.

The samples were immersed in 20% cupric sulfate for a total of 84 days. Figure 125 shows the percent weight change versus time plots for the three tests labelled 1, 2, and 3. As can be seen, samples 1 and 2 behaved consistently, but not sample 3. It appears that sample 3 lost a considerable percentage of its weight during the first 28 days of testing. It is possible that sand particles may have fallen off this sample during the first 28 days of its immersion in cupric sulfate or during the handling of the sample as it was weighed. Since the shape of the curve for sample 3 agrees for the most part with the other two curves beyond the 28th day, it was concluded that the reactivity of the three samples from this day to the end of testing was similar.

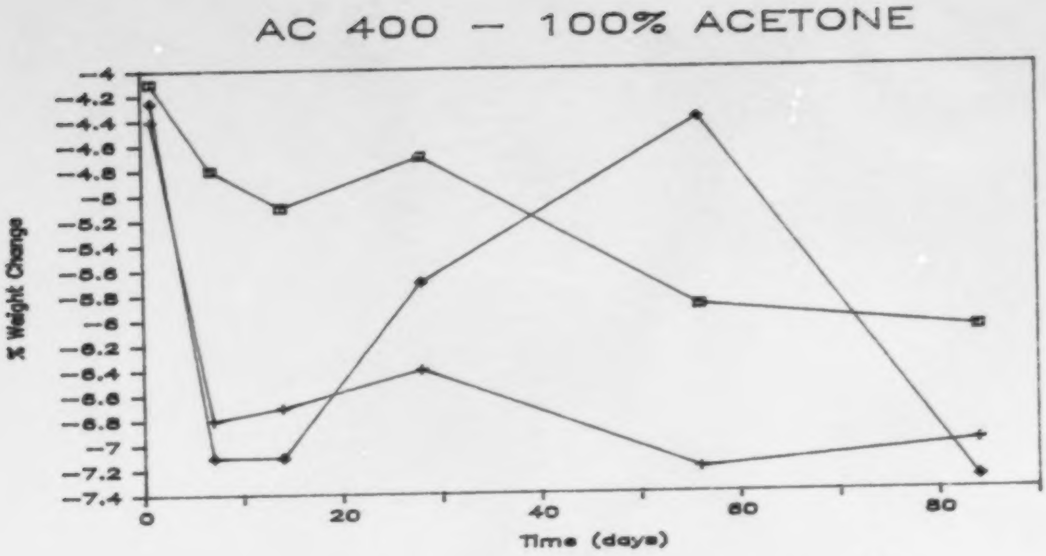


Figure 123. Percent weight change versus time plots for acrylate grout samples immersed in 100% acetone.

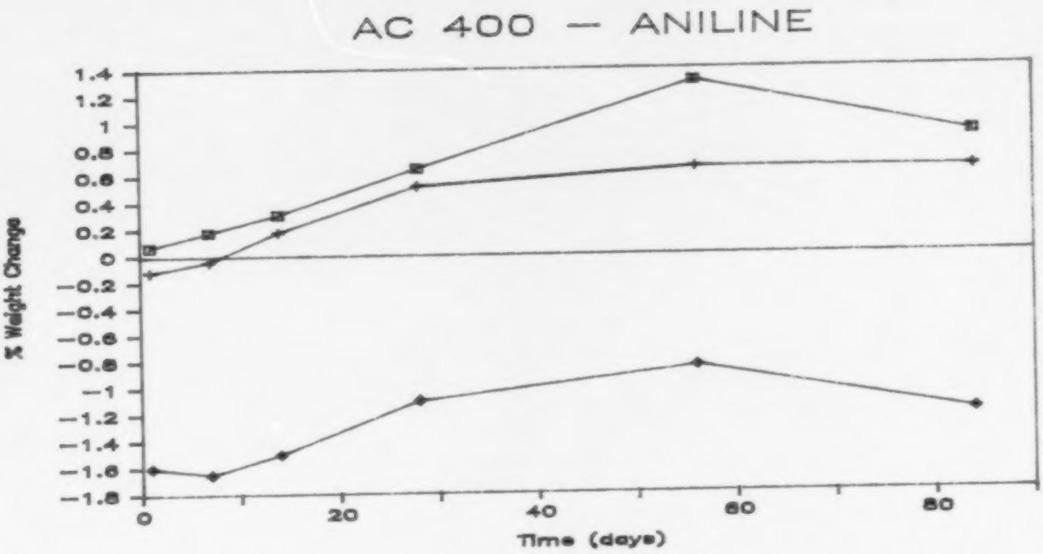


Figure 124. Percent weight change versus time plots for acrylate grout samples immersed in aniline.

Disregarding the data obtained from sample 3, the other two samples sustained an initial 1% weight increase during the first day, which was followed by a uniformly varying weight decrease all the way to the 84th day, or the end of testing. By the 84th day, samples 1 and 2 registered a net 3% decrease in their weight.

Considering the data from all three samples, the average weight gain during the first day was 0.5%, which was followed by decreases in weight that reached a 4.5% weight loss at 28 days, 4.8% at 56 days, and 7.2% at 84 days.

After 28 days of testing the initially rubberlike consistency of the samples turned hard, and after 56 days, their color became green. The samples remained hard and green to the end of the test period.

In summary, two of the three samples behaved quite consistently. The third sample (sample 3) deviated excessively from the other two during the first 28 days of testing. Based on the curves for samples 1 and 2, the average weight loss of 3% in 84 days is considered to be low. If all three samples are considered, the 7.2% average weight loss is characterized as medium low. From the shape of all three curves, it appears that the samples did not come to an equilibrium after 84 days of testing, and they indicate that with continued testing, more weight loss might have taken place.

- Reactivity Test of Acrylate Grout With 100% Ethylene Glycol

Three acrylate grout samples were tested for their reactivity to ethylene glycol. Each sample was made to the standard size of 25 mm in both diameter and thickness.

The three samples were immersed in 100% ethylene glycol for 84 days. Figure 126 shows the percent weight change versus time plots that resulted from these tests. The weight of the samples increased by an average of 2% by the end of the first day, then continued to rise slightly and reached an average maximum weight increase of approximately 2.8% by the 14th day. Continued testing resulted in a slight decrease in the average weight and the samples came to an equilibrium, at 2.6% weight gain, after 28 days of testing. Very little change occurred between the 28th and 84th day of testing.

As can be seen from the test plots, the three samples behaved quite consistently during their tests. The weight gains experienced by these three samples with 100% ethylene glycol are considered low.

The consistency of the samples changed from rubbery to hard after having been immersed in 100% ethylene glycol for 28 days and remained hard for the duration of the tests.

- Reactivity Test of Acrylate Grout With 4N Hydrochloric Acid

Three cylindrical acrylate grout samples were tested for their reactivity to 4N hydrochloric acid. The samples were 25 mm in both diameter and thickness.

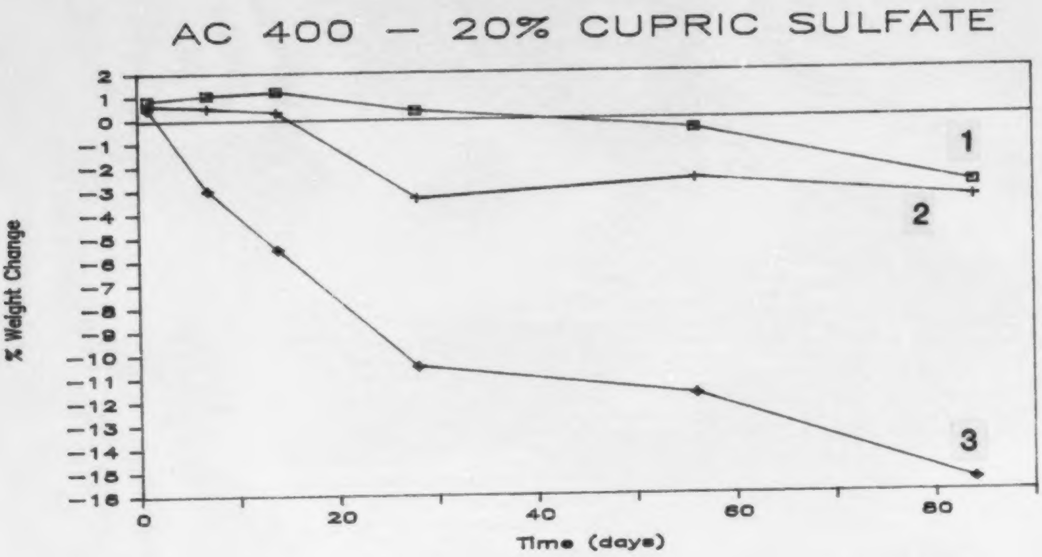


Figure 125. Percent weight change versus time plots for acrylate grout samples immersed in 20% cupric sulfate.

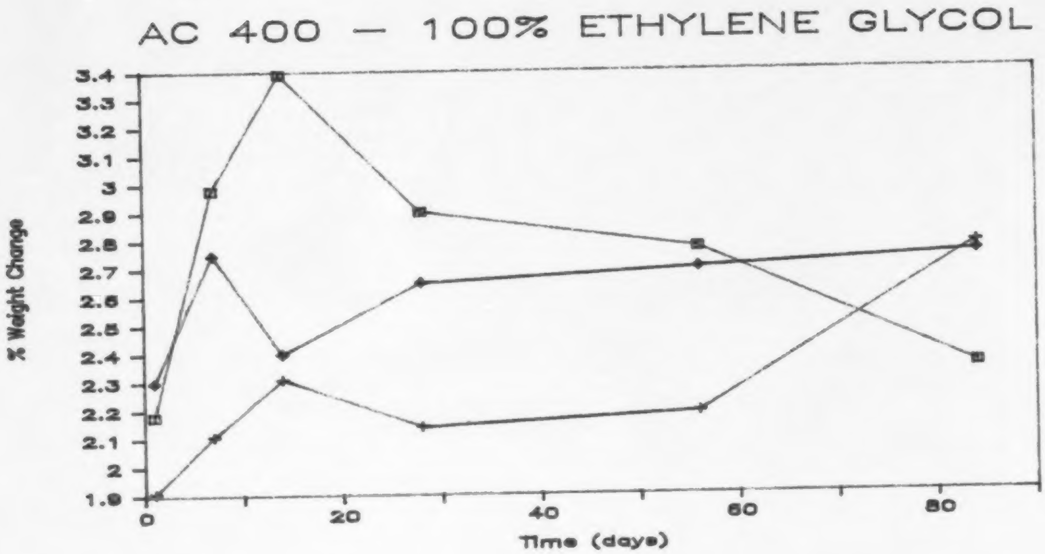


Figure 126. Percent weight change versus time plots for acrylate grout samples immersed in 100% ethylene glycol.

The acrylate grout samples were immersed in 4N hydrochloric acid for a total of 84 days. Figure 127 shows the percent weight change versus time plots drawn from the test results on the three samples. The samples exhibited practically no weight change until the 14th day of testing. Following that, the samples began to lose weight at a uniform and slow rate. After 84 days of immersion, the three samples lost an average of between 5.5 and 6% of their initial weight.

The initial rubbery consistency of the three samples softened by the 28th day of testing and remained soft through the 84th day. However, the samples did not lose their cylindrical shape.

As can be seen, the three samples behaved very consistently throughout the 84 days of testing. Their total weight loss is considered to be medium low. However, it is observed that the samples did not come to an equilibrium, and it is probable that with continued testing, the weight loss of the samples would have continued.

- Reactivity Test of Acrylate Grout With 100% Methanol

Three acrylate grout samples were tested for their reactivity with 100% methanol. All three samples were cylindrical in shape and had the same size of 25 mm in diameter and 25 mm in thickness.

The three samples were immersed in 100% methanol for a total of 84 days. The samples were removed and weighed at the prescribed periods. Figure 128 shows the percent weight change versus time plots for these samples. As can be observed, the samples lost an average of 5.5 to 6% of their initial weight by the end of the first day. With continued testing, there was little change observed until the 14th day. Following the 14th day there was a slight increase in weight to a net accumulated weight loss of 4% at the 28th day. It appears that beyond that time, the samples came to a fairly stable equilibrium, as continued testing from the 28th day to the 84th day produced little change in the weight of the samples, resulting in an average weight loss of 4.2% after 84 days of testing.

Upon immersion of the samples in 100% methanol, their rubbery consistency changed from hard to very hard within one day of testing.

As shown in Figure 128, the three samples behaved very consistently throughout their tests and came to an equilibrium by the 28th day. The weight losses suffered by the samples immersed in 100% methanol are considered to be low.

- Reactivity Test of Acrylate Grout With Real-Site Paint Waste

Three acrylate grout samples were tested for their reactivity with real-site paint waste. Each cylindrical sample was made to the standard size of 25 mm in diameter and 25 mm in thickness. The samples were immersed in the paint waste for a total of 84 days. Figure 129 shows the percent weight change versus time plots for the three samples.

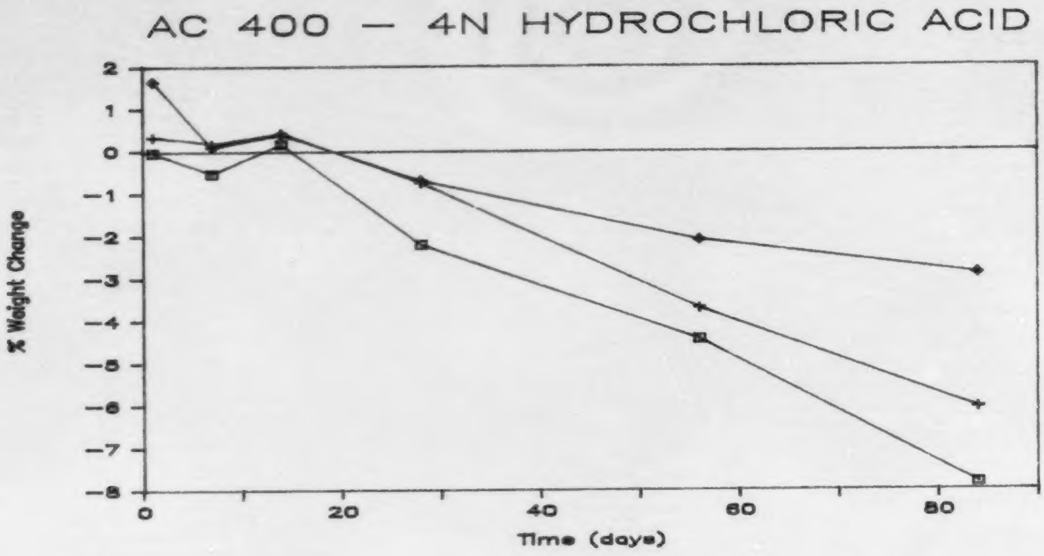


Figure 127. Percent weight change versus time plots for acrylate grout samples immersed in 4N hydrochloric acid.

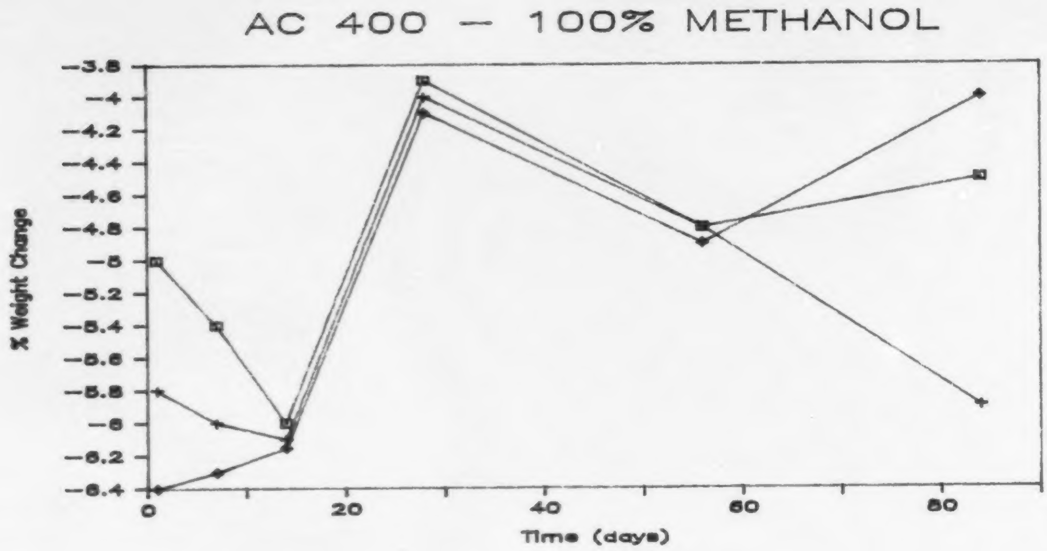


Figure 128. Percent weight change versus time plots for acrylate grout samples immersed in 100% methanol.

As shown, the samples gained an average of 5% of their initial weight by the end of the first day. This was followed by further gains yielding an average 8.4% weight increase by the end of the 7th day. At that point, the samples began to lose weight and by the 28th day of testing their weight increase was down to 0.7%. As the test continued there were further decreases in the average weight of the samples. By the 56th day the samples registered an average weight loss of 7.5%, and by the 84th day their average weight loss was 17%.

Within 1 day of their immersion into real-site paint waste, all three samples became mushy and brown in color, and remained that way to the end of the test period.

As can be seen on the test plots, the three test curves are not very consistent, however, their general trend is consistent. The 17% average weight loss suffered by the samples is considered medium high. It may be observed that the trend of weight loss that started after the 7th day did not come to an equilibrium, and one would reasonably expect that the weight loss of these samples would have continued beyond the 84th day of testing.

- Reactivity Test of Acrylate Grout With Real-Site Refinery Waste

Three acrylate grout samples were tested for their reactivity with real-site refinery waste. Each cylindrical sample was 25 mm in both diameter and thickness.

The three samples were immersed in their respective real-site refinery waste baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results from the measurements are plotted in Figure 130 as percent weight change versus time curves.

As can be seen, the test curves for samples 1 and 2 are in good agreement, however, the test curve for sample 3 deviates by as much as 20% of weight change. This may have been due to the loss of particles from sample 3, either due to the chemical or the handling of the sample. Disregarding the results from sample 3, the remaining samples exhibited an average weight increase of 4% by the end of the first day, and 8% by the end of the 7th day. After the 7th day, samples 1 and 2 began to indicate weight losses. By the 14th day, the weight losses resulted in a net decrease of 2.5%, which accumulated to a net weight loss of 20% by the 56th day of testing. At this point, the samples came to an equilibrium, and no further change occurred in their weights between the 56th and the 84th day, the end of the test period.

Within one day of their immersion into real-site refinery waste, the samples became light brown in color and within 7 days their consistency turned from hard rubber-like to very soft and mushy. After 28 days, the samples appeared to be pitted, indicating loss of grout or sand.

In summary, two of the three samples gave consistent results. While all three test curves exhibited similar shape, the weight changes of sample 3 deviated considerably from that of samples 1 and 2. Using the curves for the two samples with consistent results, the overall average decrease in weight

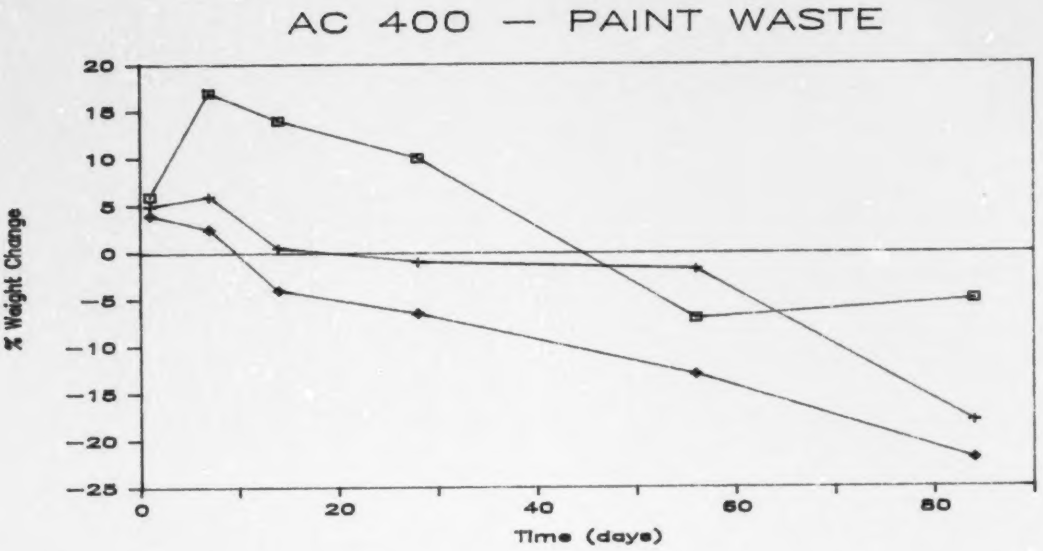


Figure 129. Percent weight change versus time plots for acrylate grout samples immersed in real-site paint waste.

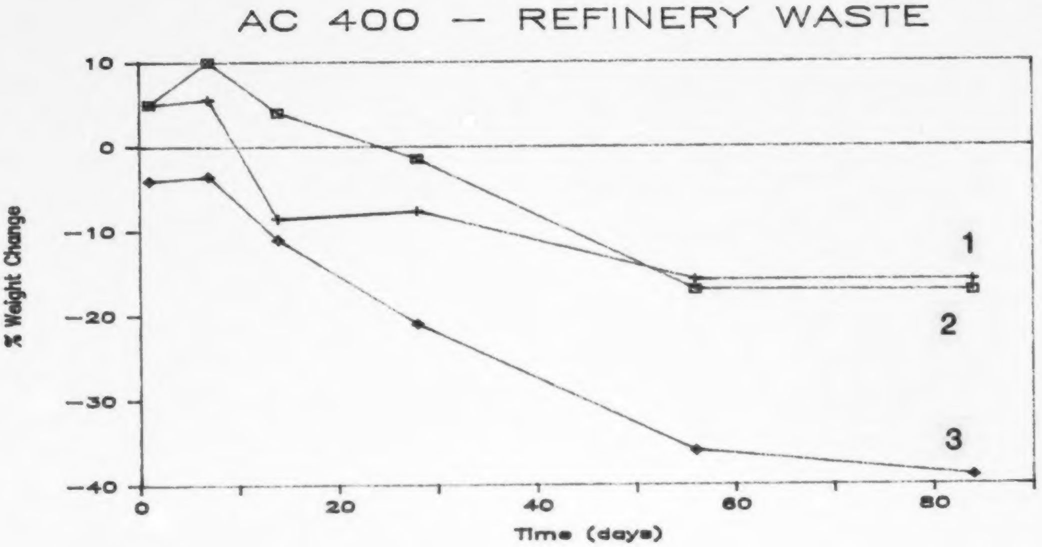


Figure 130. Percent weight change versus time plots for acrylate grout samples immersed in real-site refinery waste.

was 20%. This is considered to be a medium high to high percentage of loss. The data indicates that the samples reached equilibrium after approximately 56 days of testing.

- Reactivity Test of Acrylate Grout With 25% Sodium Hydroxide

Three acrylate grout samples were tested for their reactivity with 25% sodium hydroxide. Each cylindrically shaped sample was made to the standard size of 25 mm in both diameter and thickness. The three samples were placed in their respective 25% sodium hydroxide baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 131 as the percent weight change versus time curves.

As can be seen in Figure 131, the three samples behaved consistently. Initially the samples increased in weight, showing an average of 5.5% weight increase by the end of the first day and a 10% increase by the end of the 7th day. Following the 7th day the samples began to lose weight. By the 14th day, the samples had only an average net weight increase of 7%, which by the 28th day was reduced to 2%. By the 56th day, the samples had an average net weight loss of 3%. The trend of weight loss for the samples continued to the end of the test period. After 84 days, the samples had undergone an average 15% net weight loss. There were indications that the weight losses did not come to an equilibrium.

After 28 days of immersion in 25% sodium hydroxide, all three grout samples became soft and lost their initial shape. After 56 days they also exhibited patches of brown discolorations.

In summary, the three samples gave fairly consistent results. The overall decrease in weight for the three samples amounted to an average of 15% by the end of the 84th day. This is considered to be a medium to medium high percent weight loss. The samples did not reach equilibrium, and it appears that had the test been continued beyond the 84th day, more weight losses might have been observed.

- Reactivity Test of Acrylate Grout With Xylene

Three acrylate grout samples were tested for their reactivity with xylene. Each cylindrical sample was 25 mm in both diameter and thickness.

The three samples were placed in their respective xylene baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 132 as percent of weight change versus time curves.

The tests of the three samples resulted in test plots that are exceptionally consistent. The general shape of the curves was parabolic, that is, the initial rate of weight losses was higher than the rate at later stages of the tests. The samples lost an average of 1.7% of their weight by the end of

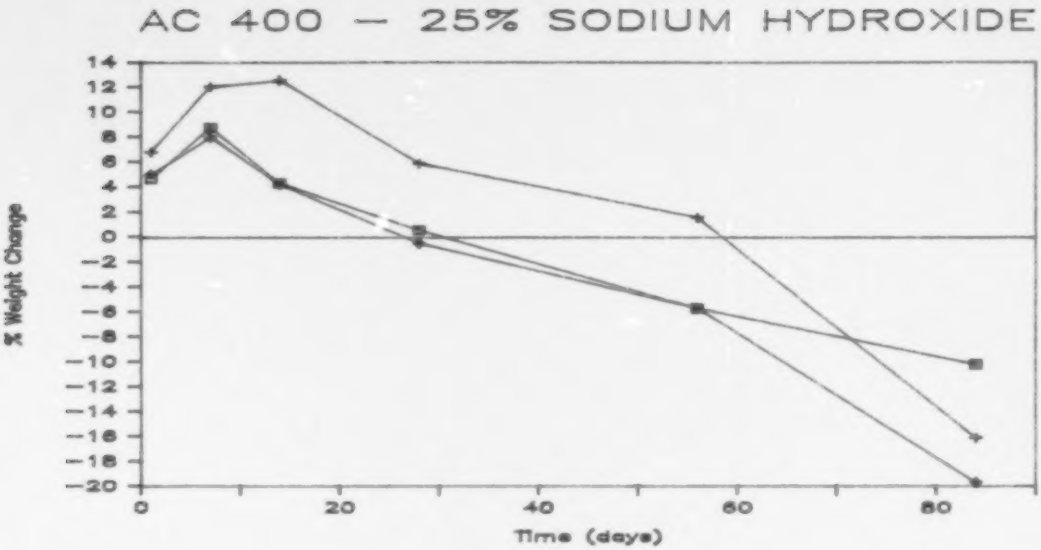


Figure 131. Percent weight change versus time plots for acrylate grout samples immersed in 25% sodium hydroxide.

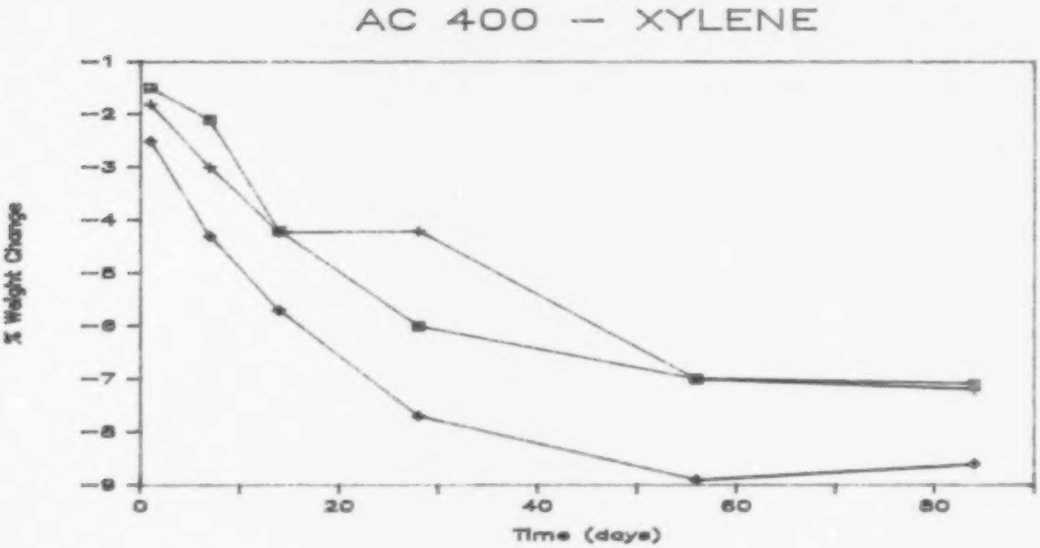


Figure 132. Percent weight change versus time plots for acrylate grout samples immersed in xylene.

the first day, 3.5% by the 7th day, and 5% by the 14th day. From there on, the weight losses were more moderate. By the 28th day, the weight loss was 6%, and by the 56th day, it leveled off at approximately 8.5%. There was practically no weight loss beyond the 56th day.

The initial hard rubber-like consistency of the samples started to deteriorate after they had been in the xylene bath for one day, and they became soft between the 14th and 28th day of testing.

In summary, the three samples yielded very consistent results. The maximum average decrease in weight was 8.5%. This is considered to be a medium low percent of loss. The weight losses for the three samples reached a virtual equilibrium after 56 days of testing.

Reactivity Tests of Cement-Bentonite (Mix 1) Grout

The cement-bentonite (mix 1) grout samples were prepared by mixing the cement, and hydrated bentonite, and water by hand and placing it in the 25 mm diameter and 25 mm high cylindrical molds. No sand was used in this mix. After having been cured, the samples had a gray color and were hard. Three replicate samples were immersed into water and into each of the following chemicals: 100% acetone, 100% methanol, real-site paint waste, real-site refinery waste, and xylene.

Due to their immersion in the above leachates, the cement-bentonite (mix 1) grout samples gained a maximum of 2.9% of their initial weight with real-site paint waste, and lost a maximum of 23% of their weight in 100% acetone.

In the following sections the reactivity of the cement-bentonite (mix 1) grout samples with water and each of the above chemicals is discussed.

○ Reactivity Test of Cement-Bentonite (Mix 1) Grout With Deionized Water

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 1) was tested with deionized water.

The three samples were immersed in their respective water baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 133 as percent weight change versus time curves.

The test plots show that the results on the three samples with water were fairly consistent, considering the scale of the drawing. The samples started out with an average weight loss of 0.5% by the end of the first day, which reversed and became an average net weight gain of 0.4% by the end of the 7th day. From the 7th day to the end of the 28th day, the samples exhibited little change. However, beyond the 28th day, they began to lose weight and ended with an average net loss of 1.5% at 84 days. This net weight loss is considered to be low. With respect to consistency, the samples maintained their initial hardness and gray color throughout the full test period. The three samples did not reach an equilibrium and it appears that had the tests been continued, more moderate weight losses might have occurred.

- Reactivity Test of Cement-Bentonite (Mix 1) Grout With 100% Acetone

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 1) was tested with 100% acetone.

The samples were immersed in 100% acetone for a total of 84 days. Weight measurements were taken at standard elapsed times during that period. Figure 134 shows the percent weight change versus time plots that resulted from the tests.

As can be observed from the test plots, the three samples behaved quite consistently up to the 56th day of testing. In particular, upon their immersion in acetone they exhibited a sudden weight loss that amounted to an average of 26% by the end of the first day of testing. After that, and for the rest of the test period, the samples remained at a fairly constant weight, with their average accumulated weight losses fluctuating between 28 and 22%. After the 56th day the plot for one of the samples was discontinued because its 84th day reading was found to be in error. The 84th day average weight of the other two samples indicated a 23% weight loss. The weight losses suffered by these samples are considered to be high to very high. The initial hard consistency of the samples did not change during their testing with acetone. The color of the samples changed from gray to white during the first day of the test.

In summary, the samples seemed to have reached fairly stable equilibrium after the first day of exposure, during which time they lost 26% of their initial weight.

- Reactivity Test of Cement-Bentonite (Mix 1) Grout With 100% Methanol

The reactivity of three standard size 25 mm in diameter and 25 mm thick cylindrical samples of cement-bentonite (mix 1) was tested with 100% methanol. The three samples were immersed in methanol for a total of 84 days. During this period, weight measurements were taken at standard time intervals. The results of the measurements on the three samples are plotted in Figure 135 as percent weight change versus time curves.

The results from the three tests are very consistent. The three samples had high weight losses during the first day of testing, amounting to an average loss of 18.5% of their initial weight. The curves indicate a further dip in weight loss at the 14th day, but the weights of the samples bounced back to a net average loss of 18% at 28 days. With continued testing the samples gained a few percentages in their weight, reaching 16% average net weight loss at the 56th day. At that time the samples came to equilibrium with respect to their weights.

The 84 day long exposure of the samples to methanol had no effect on their hard consistency and did not change their color.

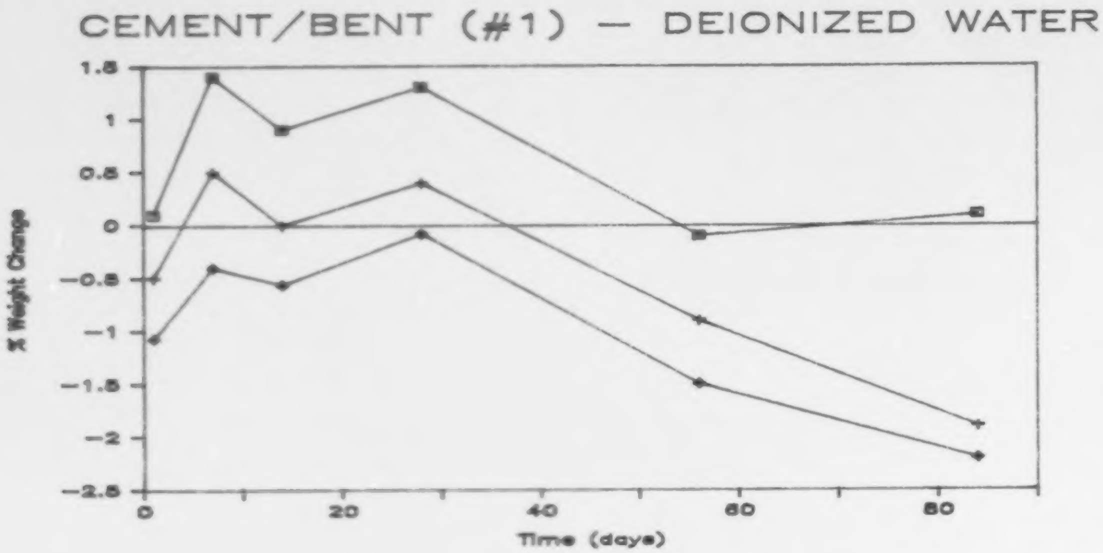


Figure 133. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in deionized water.

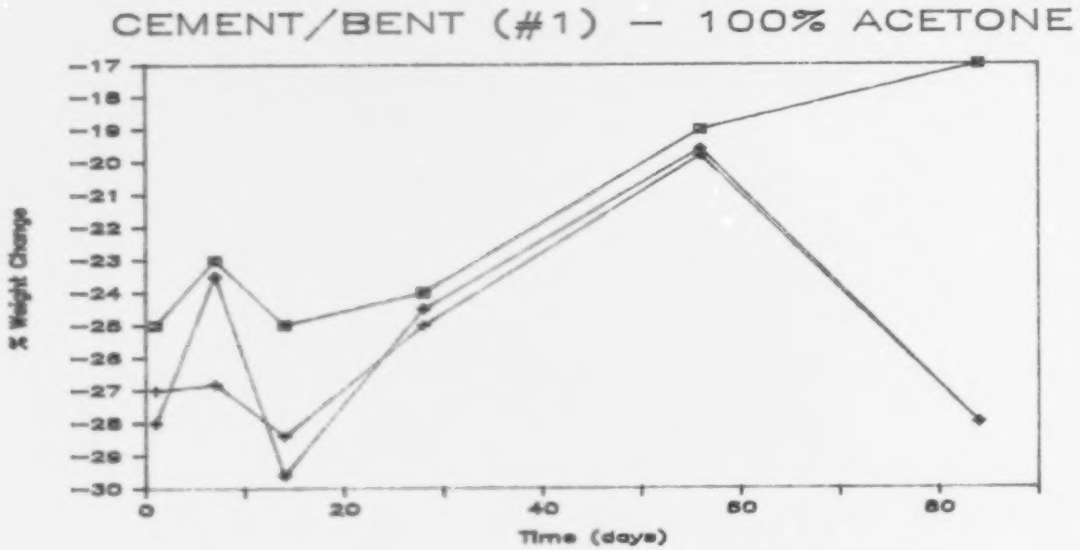


Figure 134. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in 100% acetone.

In summary, the three cement-bentonite (mix 1) samples gave exceptionally consistent results. The overall decrease in weight amounted to an average of 16% accumulated weight loss. This is considered to be a medium high percentage of loss. The change in weight of the samples reached equilibrium after 56 days of testing.

- Reactivity Test of Cement-Bentonite (Mix 1) With Real-Site Paint Waste

Three cement-bentonite (mix 1) samples were tested for their reactivity with real-site paint waste. Each cylindrical sample was of the standard size of 25 mm in diameter and 25 mm in thickness.

The three samples were immersed in paint waste for 84 days. Weight measurements were taken at standard time intervals. Figure 136 shows the percent weight change versus time plots which resulted from the testing of the samples. As can be seen, the tests gave somewhat inconsistent results. However, this inconsistency is not severe considering the scale of the drawing. Using the average weight of the three samples, their weight rose by 0.6% by the end of the first day of testing. Continued testing produced gradually increasing weights that resulted in a 1.5% average increase by the 7th day, 1.7% by the 14th day, and 2.6% weight increase by the 28th day of testing. On an average basis, there was little change in the weight of the samples beyond the 28th day of testing. Through 84 days of testing the average weight increase for the three samples was 2.9%. This average accumulated weight gain is considered to be low. It appears that the three samples practically reached equilibrium after only 28 days of testing.

The initial hardness of the samples was not changed by their 84 day long exposure to real-site paint waste. However, their color changed from gray to brownish gray after only one day of testing.

- Reactivity Test of Cement-Bentonite Grout (Mix 1) With Real-Site Refinery Waste

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 1) was tested with real-site refinery waste.

The three samples were placed in their respective real-site refinery waste baths for 84 days. Weight measurements were taken at standard time intervals. The results of the measurements are plotted in Figure 137 as percent weight change versus time curves.

As can be seen from the plots, the three reactivity tests gave fairly consistent results. There was practically no weight change of the samples by the end of the first day; by the 7th day their average weight increased by 0.9% of their initial weight. With further testing, the sample weights continued to increase and reached their peak of 1.9% weight gain after 28 days of testing. The average weight of the samples did not change perceptively beyond the 28th day.

The 84 day long exposure of the samples to refinery waste did not affect

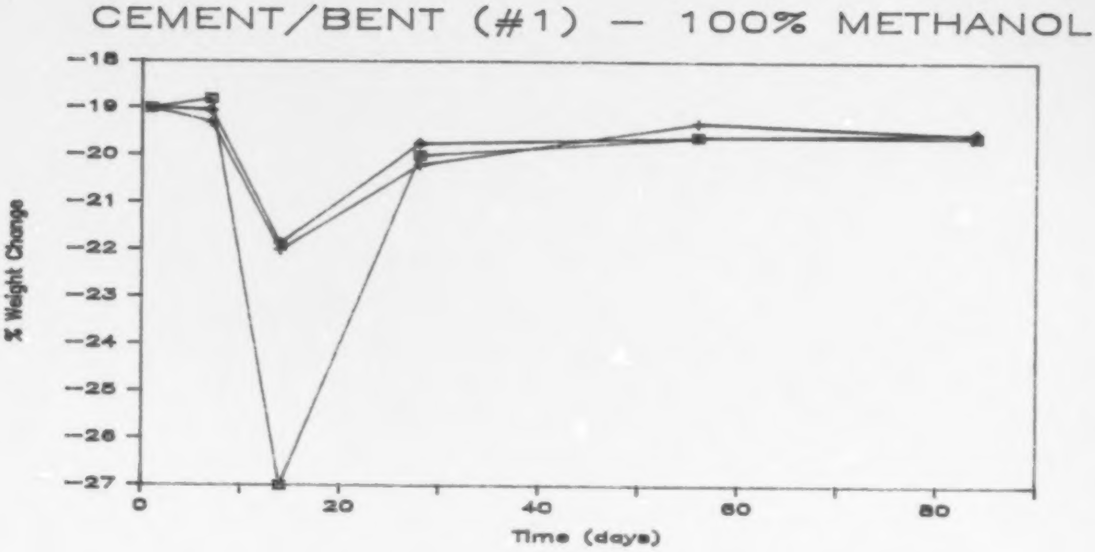


Figure 135. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in 100% methanol.

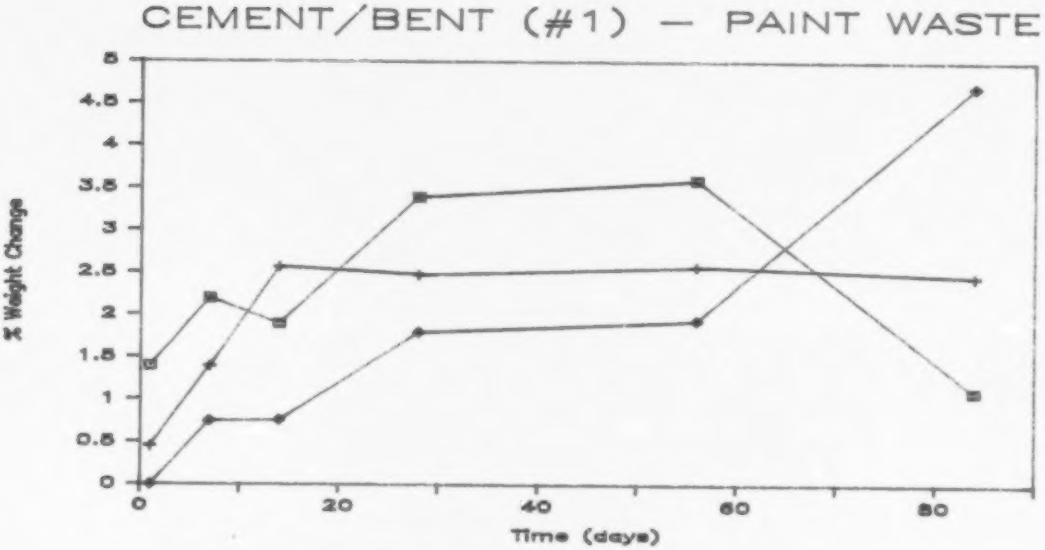


Figure 136. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in real-site paint waste.

their hardness. Their color changed from gray to brown by the end of the first day of testing, to dark brown by the 14th day, and to black by the 28th day.

In summary, the three samples gave consistent results. The final change in sample weight amounted to an average 1.9% accumulated weight gain. This is considered to be a low weight gain.

- Reactivity Test of Cement-Bentonite (Mix 1) Grout With Xylene

Three samples of cement-bentonite (mix 1) samples were tested for their reactivity with xylene. Each cylindrical sample of cement-bentonite (mix 1) was made to the standard size of 25 mm in both diameter and thickness.

The three samples were placed in their xylene baths for 84 days. Weight measurements were taken at standard time intervals. Figure 138 shows the percent weight change versus time plots that resulted from the testing of the samples. As can be seen, the samples exhibited an initial weight gain that reached an average peak of 1.7% after 7 days of testing. After the 7th day the samples began to lose weight and by the 14th day their weights had returned to their initial values. There was no weight change between the 14th and 28th days. Beyond the 28th day, the samples exhibited a continued and gradual weight loss. After the 56th day the plot for sample 2 had to be discontinued because of a bad reading at 84 days. However, the plots for samples 1 and 3 were valid, and these two samples reached an average weight loss of 4.3% by the 84th day of testing. This weight loss is considered to be low.

The 84 day long exposure of the cement-bentonite (mix 1) grout samples to xylene did not change their initial hardness, nor their gray color.

As noted above, the weight of the samples did not reach equilibrium. It appears that had the tests been continued beyond the 84th day, more weight loss might have been observed for samples 1 and 3.

Reactivity Tests of Cement-Bentonite (Mix 2) Grout

The cement-bentonite (mix 2) grout samples were prepared the same way as the cement-bentonite (mix 1) samples, except for the proportions of the components. The cured samples were gray in color and hard in consistency. Three replicate samples were immersed into each of the following chemicals: aniline, 20% cupric sulfate, 100% ethylene glycol, 4N hydrochloric acid, and 25% sodium hydroxide.

The immersion of the cement-bentonite (mix 2) grout samples in the above chemicals caused various reactions. The observed weight changes ranged from an 11.1% weight gain to a 100% weight loss. The 11.1% weight gain occurred to the samples immersed in 20% cupric sulfate, while the samples immersed in 4N hydrochloric acid underwent 100% weight loss, or total disintegration.

In the following sections the behavior of the cement-bentonite (mix 2)

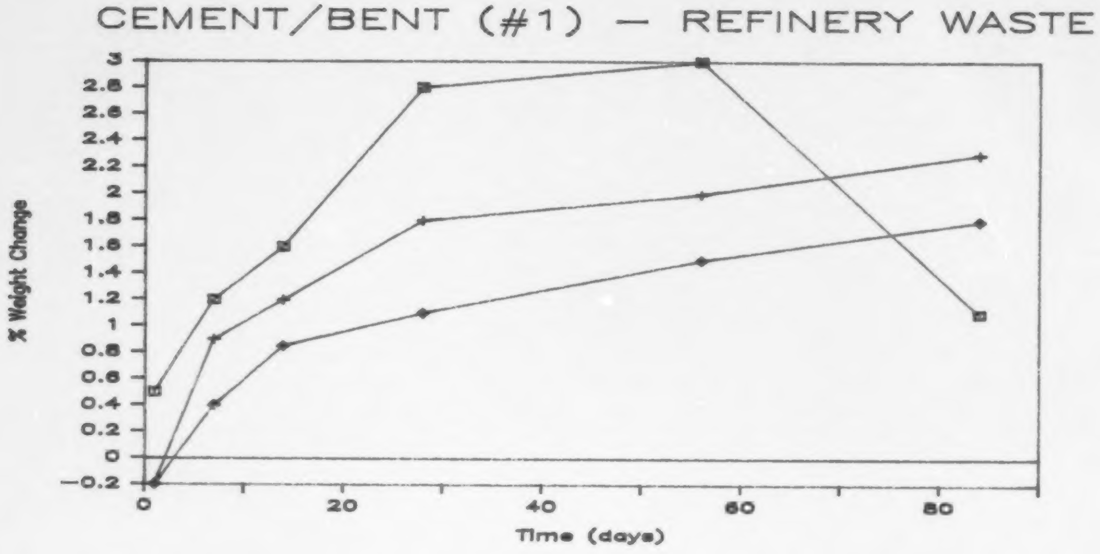


Figure 137. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in real-site refinery waste.

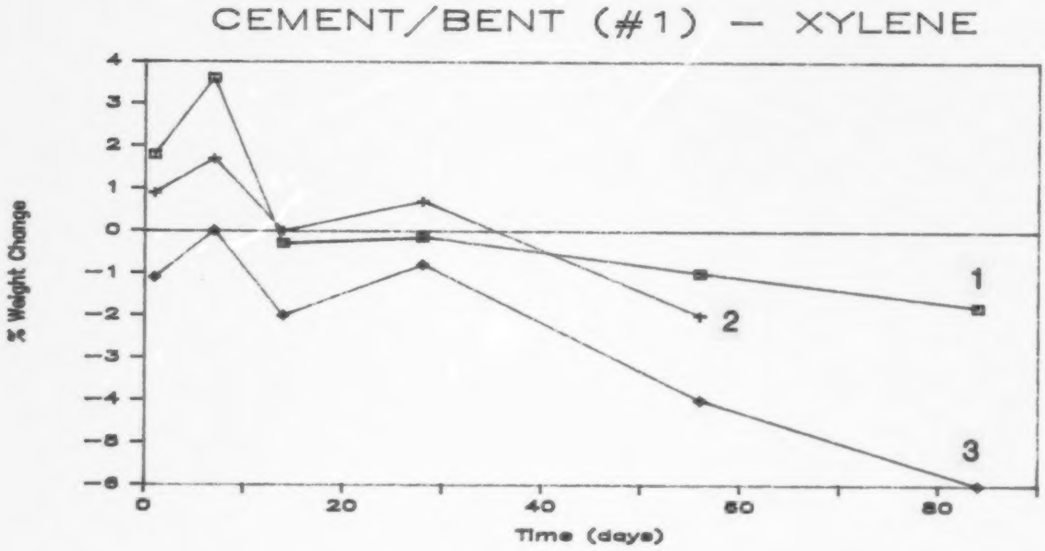


Figure 138. Percent weight change versus time plots for cement-bentonite (mix 1) grout samples immersed in xylene.

grout with the various chemicals is described.

- Reactivity Test of Cement-Bentonite (Mix 2) Grout With Aniline

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 2) was tested with aniline.

The three samples were placed in their respective aniline baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results are plotted in Figure 139 as percent weight change versus time curves.

The test plots indicate that results from the three samples are quite consistent. Following their immersion in aniline, the three samples underwent weight increases that averaged 2.3% during the first day of testing. This was followed by further increases averaging 3.5% at 7 days and 3.8% at 14 days. After the 14th day of testing the weight of the samples came to an equilibrium. The average net weight increases were 3.9%, 4.1% and 4.0% at 28, 56, and 84 days, respectively. The final value of 4.0% weight increase is considered to be low. It is reasonable to assume that the samples reached a final equilibrium somewhere between the 14th and 28th day of the test period.

During the test with aniline, there was no change in the hardness of the samples. However, their color changed from gray to black and dark brown by the 56th day of testing.

- Reactivity Test of Cement-Bentonite (Mix 2) Grout With 20% Cupric Sulfate

Three samples of cement-bentonite (mix 2) were tested for their reactivity to 20% cupric sulfate. Each cylindrical sample was 25 mm in diameter and 25 mm in thickness.

The samples were placed in 20% cupric sulfate baths for 84 days. Weight measurements were taken at standard time increments. Figure 140 shows percent weight change versus time plots that resulted from the testing of the three samples. The plots show that all three samples gained weight by the end of the first day of testing. Their average weight increase was 2.5%. Following that, sample 1 continued to gain weight, while samples 2 and 3 lost weight until the 14th and 7th days, respectively. The weight loss of samples 2 and 3 may have been due to the loss of small pieces or sand particles that may have fallen off the samples during the initial stages of immersion or during the weighing operations. Beyond the 14th day of testing, all three samples exhibited a trend of weight gain which continued to the end of the test period. After 84 days of testing, the average gain in weight for the three samples was 11.1%. This is considered to be a medium level weight gain. As shown by the test plots, these samples did not reach equilibrium, and it appears that had the tests been continued, further changes in weight might have been observed.

With respect to their consistency, the initial hardness of the samples

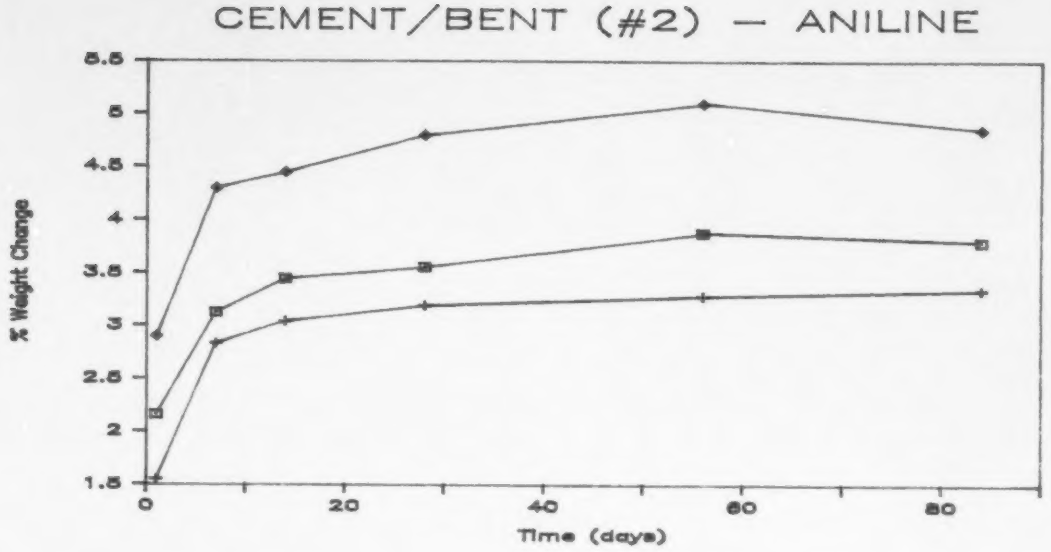


Figure 139. Percent weight change versus time plots for cement-bentonite (mix 2) grout samples immersed in aniline.

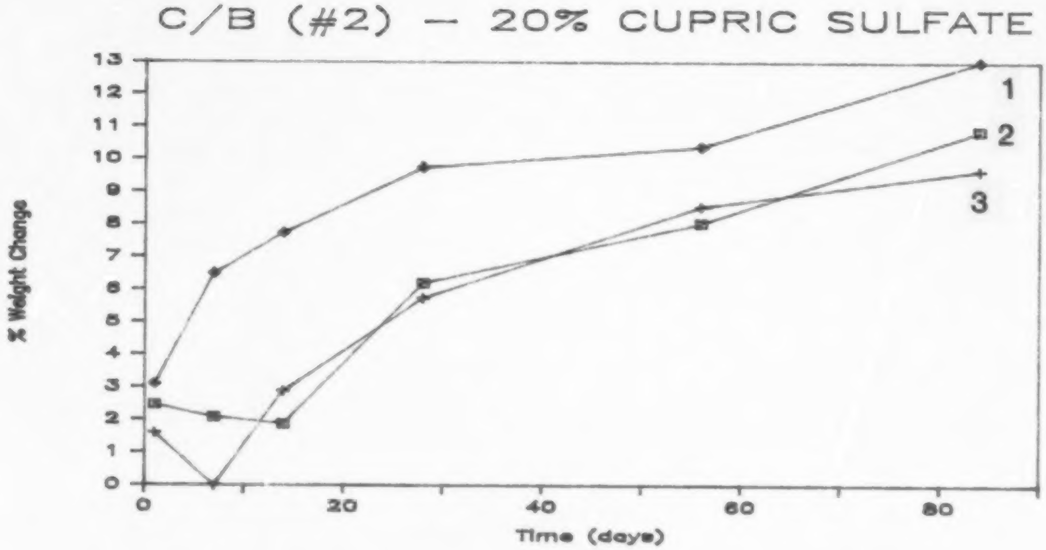


Figure 140. Percent weight change versus time plots for cement-bentonite (mix 2) grout samples immersed in 20% cupric sulfate.

did not change in 56 days of testing, but by the 84th day they softened slightly. Also, by the 28th day the surface of the samples had a milky appearance, and by the 56th day their color had turned green with black spots.

- Reactivity Test of Cement-Bentonite (Mix 2) Grout With 100% Ethylene Glycol

Three samples of cement-bentonite (mix 2) were tested for their reactivity with 100% ethylene glycol. Each cylindrical sample was 25 mm in diameter and thickness.

The three samples were placed in their respective ethylene glycol baths for 84 days. Their weights were measured at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements are plotted in Figure 141 as percent of weight change versus time curves. As can be seen, the test plots for the three samples are not very consistent, since the curves are spread far apart. However, the overall shapes of the curves are very similar. Using average values, it is observed that the samples increased markedly in weight (an average of 6%) during their first day of immersion in ethylene glycol. With continued testing, the trend of weight increase continued to the 14th day, at which time the average gain in weight amounted to 9.9%. Thereafter the weight of the samples began to fall very gradually and terminated at an average value of 8.2% accumulated weight increase after 84 days of testing. The 8.2% final weight increase is considered to be medium low. As can be seen from the test plots, the three cement-bentonite samples in ethylene glycol did not reach complete equilibrium.

The initial hard consistency and gray color of the samples were not affected by their exposure to ethylene glycol.

- Reactivity Test of Cement-Bentonite (Mix 2) Grout With 4N Hydrochloric Acid

Three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 2) were tested for their reactivity with 4N hydrochloric acid.

The three samples were immersed in the hydrochloric acid for a total of 84 days. Their weights were measured at the standard time intervals. The results of these measurements are plotted in Figure 142 as percent weight change versus time curves. As indicated by the plots, all three samples suffered high weight losses during the first day of immersion, as they each lost close to 50% of their initial weight. The average weight loss increased to 62% by the end of the 7th day. The samples lost weight due to breakage and spalling, while the remaining core portions kept their hard consistency. With continued testing, both samples 1 and 2 completely broke apart, sample 1 after the 14th day and sample 2 after the 28th day of testing. For some unknown reason, sample 3, after having lost some 62% of its weight by the 7th day of testing, underwent relatively minor weight losses for the rest of its test. After 84 days of testing, sample 3 lost 69% of its original weight. It became small, but was still hard. Based on the performance of samples 1 and 2, one would anticipate that had the test on sample 3 been continued beyond 84 days, it too might have disintegrated. Clearly, the effect of

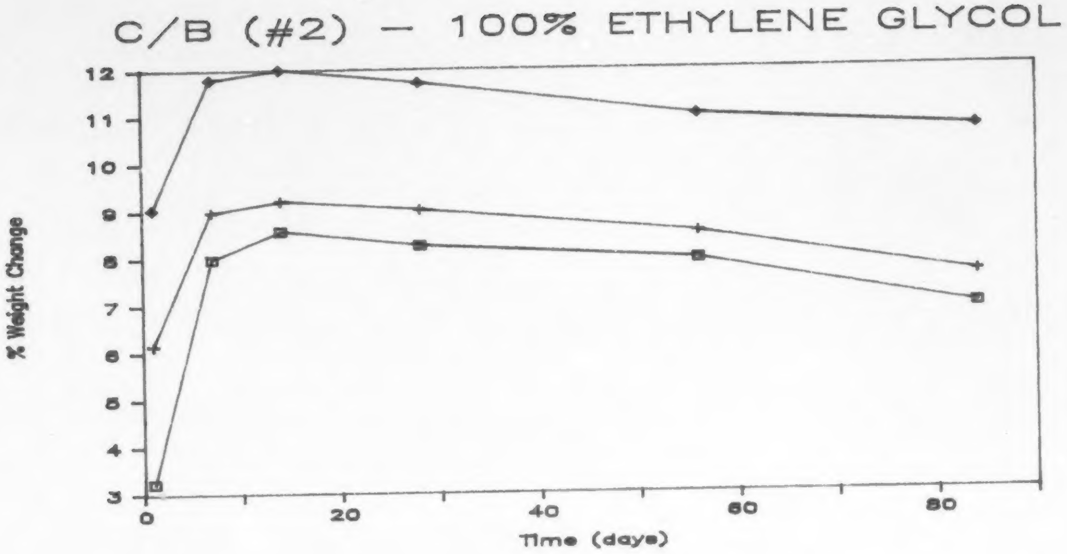


Figure 141. Percent weight change versus time plots for cement-bentonite (mix 2) grout samples immersed in 100% ethylene glycol.

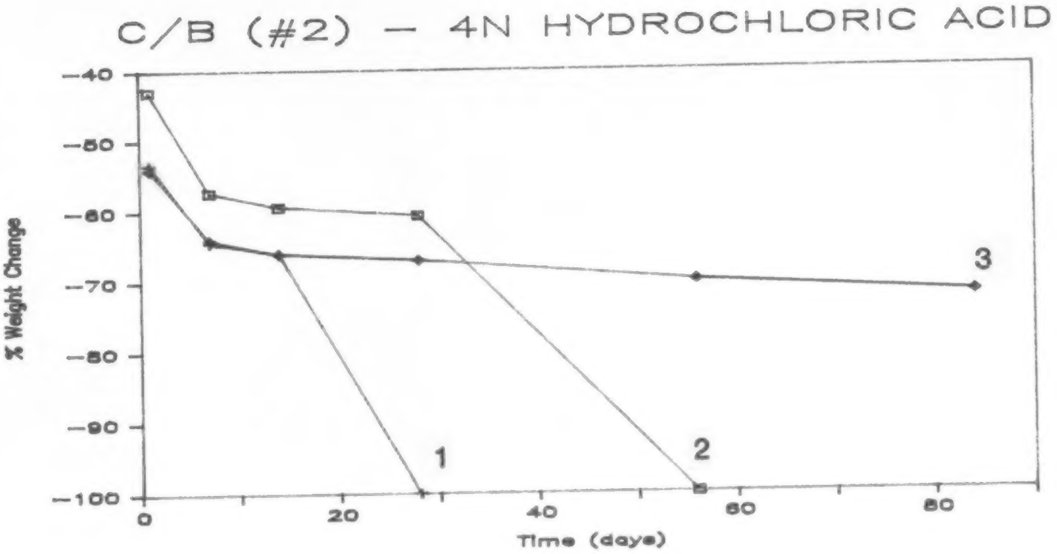


Figure 142. Percent weight change versus time plots for cement-bentonite (mix 2) grout samples immersed in 4N hydrochloric acid.

4N hydrochloric acid on the cement-bentonite (mix 2) samples was extremely detrimental.

- Reactivity Test of Cement-Bentonite (Mix 2) Grout With 25% Sodium Hydroxide

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of cement-bentonite (mix 2) was tested with 25% sodium hydroxide.

The three samples were placed in their respective sodium hydroxide baths for 84 days. Weight measurements were taken at the standard time intervals of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 143 as percent weight change versus time curves.

The plots show that the three samples behaved very consistently. On an average weight basis, the samples underwent a net weight increase of 13.5% by the end of the first day. The weights decreased slightly to an average weight gain of 12.5% by the 7th day and 6% by the 14th day. With continued testing, the samples kept losing weight, and by the 84th day an average weight loss of 21% was recorded.

The initial hard consistency of the core of the samples did not change during the 84 day test period, but the surface layers did get sticky and soft, as the samples got smaller in both size and weight following the first day. This suggests that some surface dissolution of the grout may have taken place. There was no change in the color of the samples.

In conclusion, the three samples gave exceptionally consistent results. The total decrease in weight amounted to an average of 21%. This is considered to be a high percentage of loss. The samples did not reach an equilibrium weight, and it appears that had the tests been continued beyond the 84th day, more weight loss might have been observed.

Reactivity Tests of Urethane Grout

The urethane grout samples were prepared essentially the same way as the acrylate grout samples. The cured samples were grayish white and felt like medium hard rubber. Three replicates were immersed into water and into each of the ten types of chemicals used with the acrylate grouts.

The urethane grout samples registered a maximum percent weight gain of 45% during 28 days of immersion in aniline. The samples underwent their maximum weight loss of 20% while immersed in xylene.

In the sections that follow, the reactions of urethane grout with water and specific chemicals are discussed.

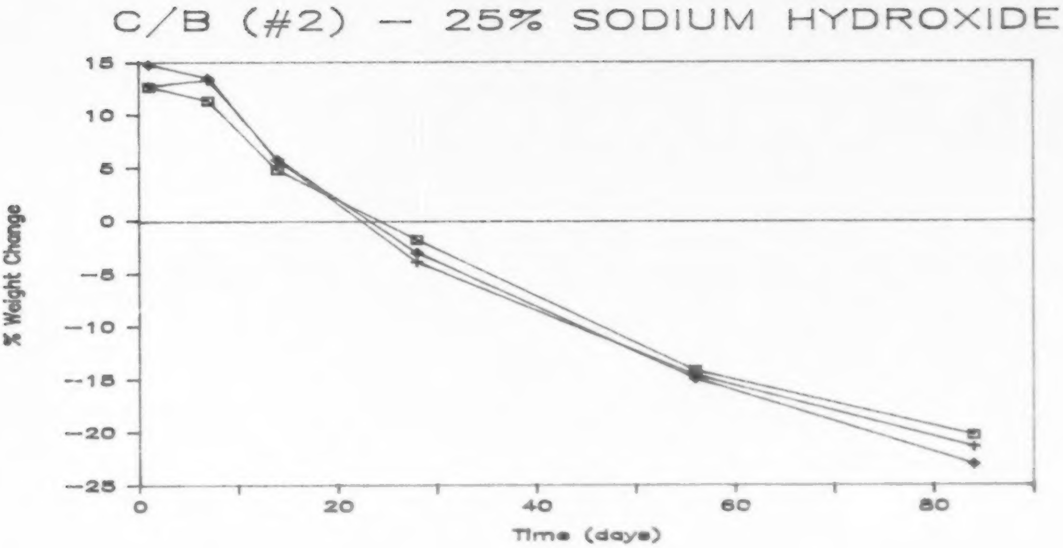


Figure 143. Percent weight change versus time plots for cement-bentonite (mix 2) grout samples immersed in 25% sodium hydroxide.

◦ Reactivity Test of Urethane Grout With Deionized Water

The reactivity of three standard size 25 mm diameter and 25 mm thick cylindrical samples of urethane was tested with deionized water.

The three samples were immersed in their respective water baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the tests on the three samples are plotted in Figure 144 as percent weight change versus time curves.

Even though the three test curves indicated large percent weight changes, the curves showed remarkable similarity. After only one day of immersion in water, the three urethane samples underwent a 23% increase in their weight, and after 7 days of testing reached a peak of 48% weight gain. Following that, the samples lost weight as their weight increase dropped to 30% after 14 days of testing. Between the 14th and the 28th day the average weight of the samples again increased slightly to a value of 36%. These were the last readings, since the samples became so soft after the 28th day that they lost their shape and could not be weighed.

Within one day of immersion of the urethane grout samples into deionized water, the samples swelled and changed their consistency from rubbery to very soft. The samples continued to soften until the 28th day, when they began to lose their shape. By the 56th day the samples became semi-liquid, completely lost their shape and spread out in their beakers.

In summary, the three urethane samples in deionized water gave consistent results. The overall increase in weight amounted to an average accumulated weight gain of 36%. This is considered to be a very high percent of weight change. The weight of the three samples never reached equilibrium, since between the 28th and 56th day of testing the samples became semi-liquid, lost their shape, and could not be weighed on the 56th day.

◦ Reactivity Test of Urethane Grout With 100% Acetone

The reactivity of three standard size 25 mm diameter and 25 mm thick cylindrical samples of urethane was tested with 100% acetone.

The three samples were placed in their respective acetone baths for 84 days. Weight measurements were taken at standard elapsed times. The results of the measurements are plotted in Figure 145 as percent weight change versus time curves. The curves representing the three test results are quite consistent. By the end of the first day of testing, the samples had an average weight increase of about 1%. Following that, the samples began to lose weight, and by the end of the 7th day they lost an average of 2.5% of their initial weight, and by the end of the 14th day, 6%. The weight losses bottomed out temporarily after 28 days of testing. From there on the weight losses rebounded somewhat and at the 56th day the average weight loss was 5.5%.

The tests continued to 84 days, however, the results obtained that day were invalidated because the acetone bath had evaporated and the samples had

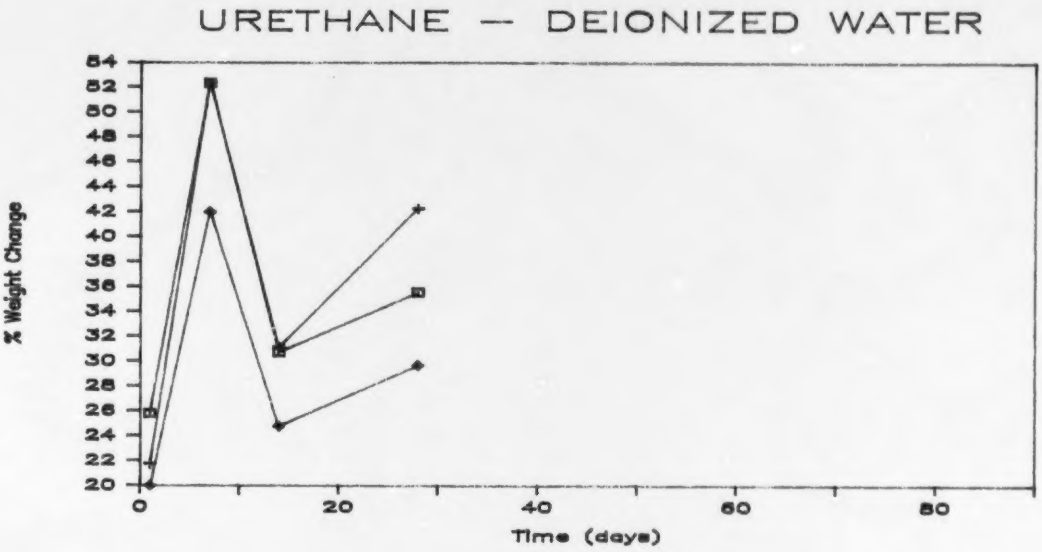


Figure 144. Percent weight change versus time plots for urethane grout samples immersed in deionized water.

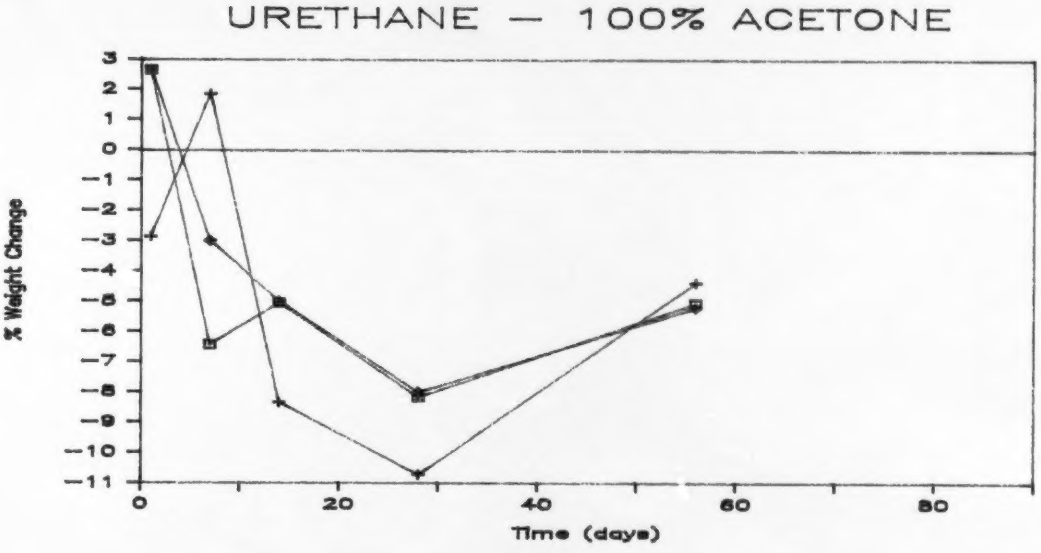


Figure 145. Percent weight change versus time plots for urethane grout samples immersed in 100% acetone.

dried in their beakers.

The initial rubbery consistency of the samples changed to very soft after only one day in the acetone bath. Two of the samples maintained their cylindrical shape. The third sample lost its shape but did not disintegrate. These conditions prevailed to the end of the tests.

In summary, the three samples gave fairly consistent results with 100% acetone. Their overall average weight loss amounted to 5.5% of their initial weight. This loss is considered to be medium low. It is judged that the weight of the samples did reach equilibrium.

- Reactivity Test of Urethane Grout With Aniline

Three urethane samples were tested for their reactivity with aniline. The samples were cylindrical in shape and were 25 mm both in diameter and thickness.

The three samples were immersed in aniline for a total of 28 days and their weights were measured at standard time increments. Figure 146 shows the percent weight change versus time plots for the three samples. As can be seen from the plots, the results were fairly consistent up until the 14th day, beyond which the weight of one sample deviated from that of the other two. After their immersion into aniline, the three samples underwent a 9% average weight increase by the first day, a 20% increase by the 7th day, and a 36% increase by the 14th day. Beyond that, the rate of weight increase slowed down and, by the 28th day, reached an average weight gain of 45%. By the 56th day the samples became semi-liquid and could not be weighed. Therefore, there are no data points beyond the 28th day of testing.

With the immersion of the urethane grout samples into aniline they gradually softened, and by the 56th day of testing they lost their shape, transformed into a glue-like consistency, and spread out in their beakers.

In summary, the three samples gave consistent results up to the 14th day. Beyond that, the behavior of one of the samples deviated from that of the other two. The total weight change amounted to an average of 45% weight gain. This occurred after 28 days of testing. This weight gain is considered to be very high. The samples became glue-like after 28 days in aniline.

- Reactivity Test of Urethane Grout With 20% Cupric Sulfate

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of urethane was tested with 20% cupric sulfate.

The three samples were placed in their respective cupric sulfate baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 147 as percent weight change versus time curves.

In this test series, the three samples underwent relatively small weight changes and the results from the three tests are consistent.

During the first day of testing, the samples lost an average of 1% of their weight. After the first day, the samples showed a trend of increasing weight. Between the 7th and 28th day, the samples exhibited an average accumulated weight loss ranging from 0.4 to 0.7%. By the 56th day the samples gained a total of 0.3% of their initial weight, and by the 84th day the gain was essentially reduced to zero. It is reasonable to assume that at the end of the test period the weight of the samples reached equilibrium.

The immersion of the urethane samples in 20% cupric sulfate caused their original off-white color to change to green. Their initial rubber-like consistency slowly changed to slightly softer by the 84th day of testing. There was no discernible change in the cylindrical shape of the samples.

In conclusion, the three samples gave consistent results. The maximum weight loss occurred after the first day of testing and amounted to an average of 1% of the initial weight of the samples. This loss is considered to be low. These samples essentially reached equilibrium after 84 days of testing. The equilibrium weight loss was near zero.

○ Reactivity Test of Urethane Grout With 100% Ethylene Glycol

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of urethane was tested with 100% ethylene glycol. The three urethane grout samples were immersed in their respective 100% ethylene glycol baths for a total of 84 days. Weight measurements were taken at standard elapsed times. The results of the measurements on the three samples are plotted in Figure 148 as percent of weight change versus time curves. As can be seen, the weight changes were relatively small and the samples behaved quite consistently.

During the first day of testing, the three samples lost an average of 0.6% of their initial weight. This was reversed in the next six days, as the samples registered an accumulated net weight gain of 0.9% by the 7th day of testing. This was followed by a slight decrease in their weight gain to 0.6% at 14 days which remained constant through the 28th day of testing. Beyond the 28th day, the samples exhibited a fairly stable condition, in that the average percent weight gain essentially remained between 0.6 and 0.25%. The weight gains of the samples essentially came to an equilibrium at that time.

Due to their immersion in 100% ethylene glycol, the rubber-like consistency of the samples became stiffer by the end of the first day of testing, and hard by the 7th day. The samples stayed hard for the remainder of the tests.

In summary, the three samples gave consistent results. The samples lost an average of 0.6% of their weight during the first day, but ended up with an average net gain in weight of between 0.6 and 0.25%. These weight changes are considered to be low. It appears that the samples reached equilibrium by the 28th day of testing.

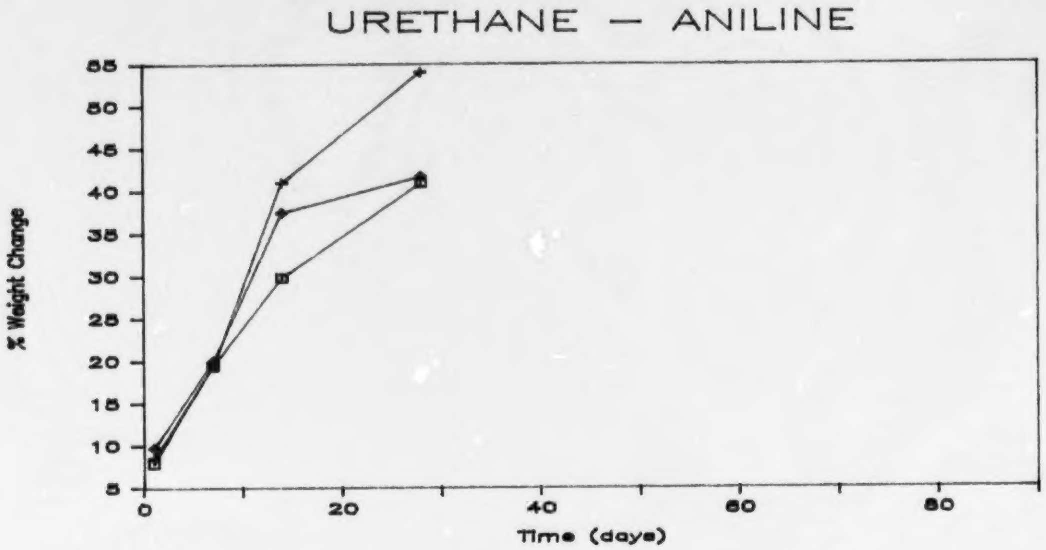


Figure 146. Percent weight change versus time plots for urethane grout samples immersed in aniline.

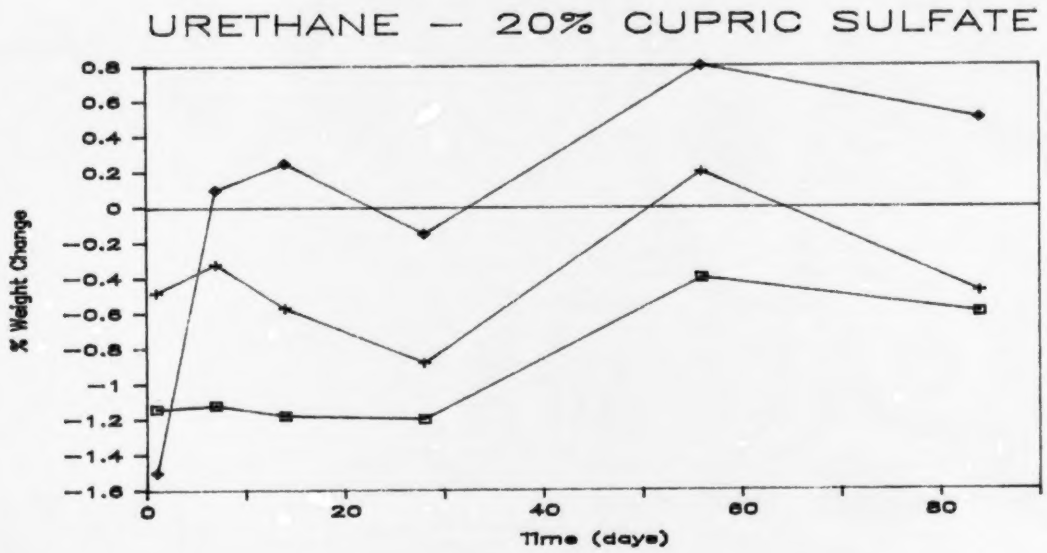


Figure 147. Percent weight change versus time plots for urethane grout samples immersed in 20% cupric sulfate.

○ Reactivity Test of Urethane Grout With 4N Hydrochloric Acid

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of urethane was tested with 4N hydrochloric acid. The three samples were placed in their respective hydrochloric acid baths for 84 days and their weights were measured at standard elapsed times. The results of these are plotted in Figure 149 as percent weight change versus time curves.

As can be seen, test results were consistent until the 28th day. Overall, during the first 28 days the samples did not react in a significant way to the 4N hydrochloric acid, namely, the percent weight changes were between positive 0.4% and negative 0.1% during that period. After the 28th day, the samples began to gain weight at a fast rate. By the 56th day, samples 1 and 2 reached an average weight increase of 3.7% (the reading on sample 3 was in error). After 84 days all three samples exhibited medium weight increases, and the average was 10.2%. By this time, the samples were quite soft, sticky and their consistency was pudding-like. It was difficult to weigh them.

In summary, the test results were fairly consistent. Up until the 28th day of testing the samples showed little reaction to 4N hydrochloric acid. After that, the weight of the samples began to rise rather quickly, and by the 84th day they reached a medium weight gain. The weight of the samples did not reach an equilibrium. The weight increases were accompanied by softening of the samples; they became soft, sticky and pudding-like in consistency.

○ Reactivity Test of Urethane Grout With 100% Methanol

Three urethane samples were tested for their reactivity with 100% methanol. Each cylindrical-shaped sample was 25 mm in diameter and 25 mm in thickness.

The three samples were placed in their respective 100% methanol baths for a duration of 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. Figure 150 shows the percent weight change versus time plots that resulted from the testing of the three samples.

As can be seen, the test plots for the individual samples are not very consistent, however, the deviations are moderate. Considering the average behavior of the three samples, one may observe that by the first day the samples had undergone a 4.2% weight increase, followed by a gradual decrease in weight which reached a net weight loss of 1.0% at 28 days. Following that, the average change [illegible] weight for the three samples fluctuated between the values of negative 0.4 and negative 0.1%. The average weight loss of the three samples was 0.1% at 84 days.

The rubber-like consistency of the three urethane grout samples became soft and very sticky by the 14th day of testing. The softening of the samples continued with further testing, and after 84 days they had a jellylike

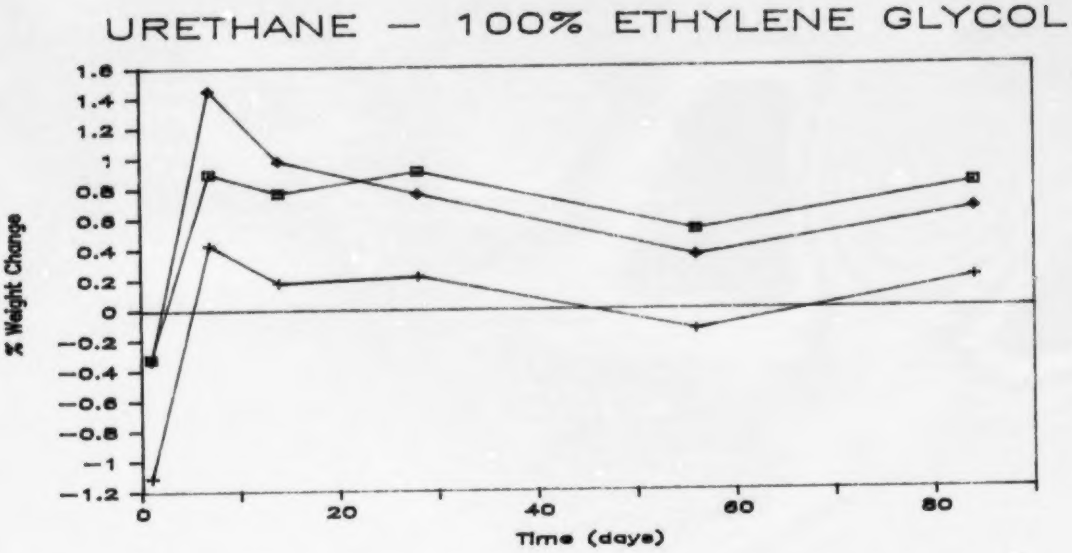


Figure 148. Percent weight change versus time plots for urethane grout samples immersed in 100% ethylene glycol.

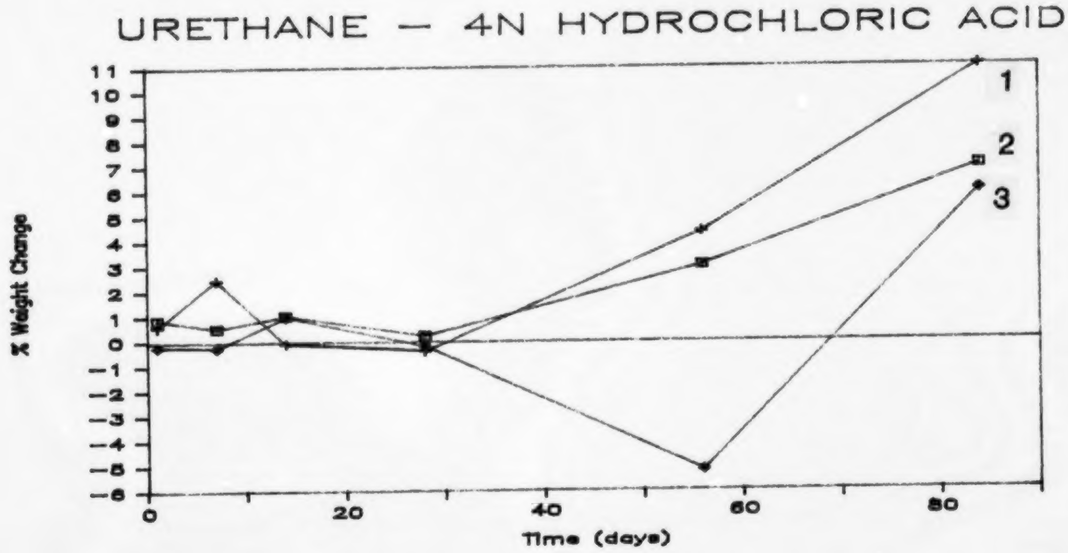


Figure 149. Percent weight change versus time plots for urethane grout samples immersed in 4N hydrochloric acid.

consistency.

In summary the three samples gave only moderately consistent results. The final decrease in weight amounted to an average of 0.1% accumulated weight loss, a negligible amount. On an average basis, the samples reached an equilibrium weight loss of between 0.4 and 0.1% after 56 days of testing.

- Reactivity Test of Urethane With Real-Site Paint Waste

The reactivity of three standard size 25 mm diameter and 25 mm thick cylindrical samples of urethane was tested with real-site paint waste.

The three samples were placed in their respective paint waste baths for 84 days. Weight measurements were taken at standard elapsed times. The results of the measurements on the three samples are plotted in Figure 151 as percent weight change versus time curves.

As can be observed from the test plots, the test results were only moderately consistent. The shapes of the curves were the same, but the weight gains of sample number 3 past the 7th day were about 2% greater than those of samples 1 and 2. On the average, the three samples gained 1% in weight by the end of the first day, 3.3% by the end of the 7th day, and 4.6% by the 14th day. This weight gain remained constant until the 28th day, then dropped off to 3.5% by the 56th day. From the 56th day to the end of the test period there were only minor changes in the weight of the samples. The three samples had an average accumulated weight gain of 3.8% at 84 days.

The immersion of the urethane grout samples in real-site paint waste changed the consistency of the samples only slightly. After 7 days the samples became spongy and remained that way to the end of the tests. Also, their color changed from white to brown by the 28th day of testing.

In summary, the three samples gave only moderately consistent results. The weight gain of sample 3 deviated from samples 1 and 2 past the 7th day. On the average the samples came to an equilibrium in their weight gain after approximately 56 days of testing, beyond which their weight gain stabilized between 3.5 and 3.8%. This weight gain is considered to be low.

- Reactivity Test of Urethane Grout With Real-Site Refinery Waste

Three samples of urethane grout were tested for their reactivity with real-site refinery waste. Each sample was cylindrical in shape and was 25 mm in both diameter and thickness.

The three samples were immersed in their respective real-site refinery waste baths for a total of 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements are plotted in Figure 152 as percent weight change versus time curves.

As can be seen from the test plots, the behavior of the samples was consistent throughout the test period. They exhibited uniform weight gains

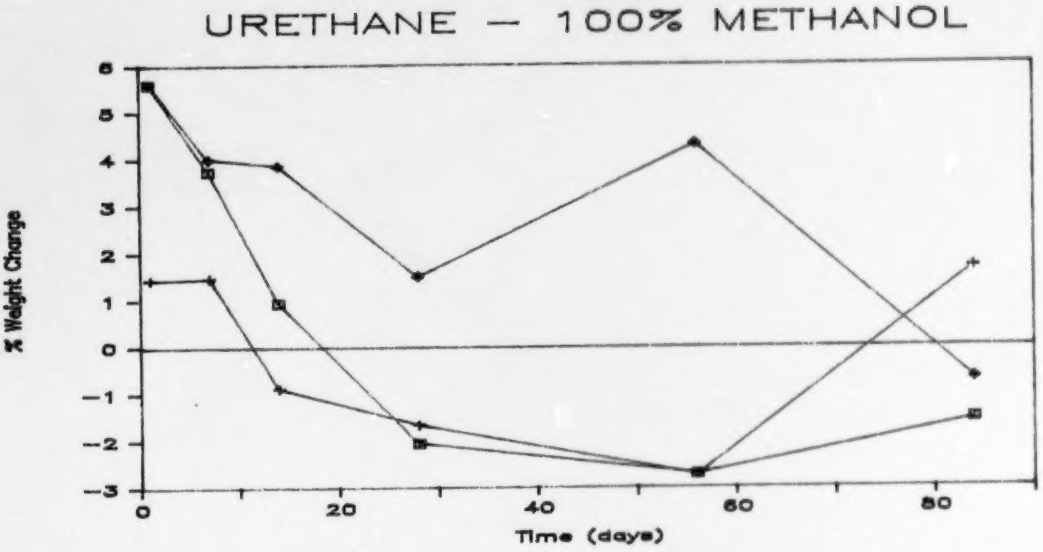


Figure 150. Percent weight change versus time plots for urethane grout samples immersed in 100% methanol.

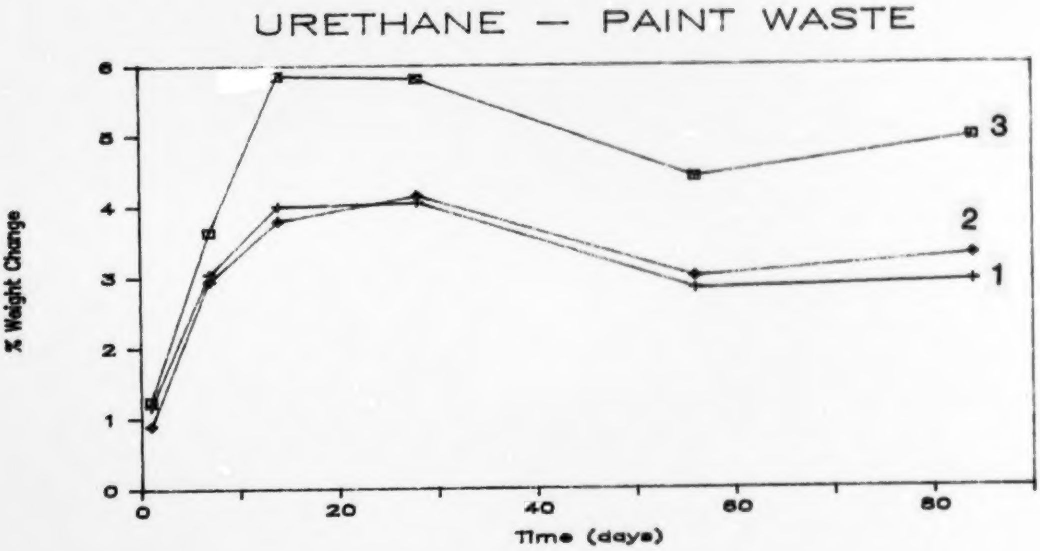


Figure 151. Percent weight change versus time plots for urethane grout samples immersed in real-site paint waste.

for the first 14 days of testing. At the 14th day they reached an average weight gain of 3.3%, then the test plots leveled off and stayed approximately at this average weight gain until the 28th day. From the 28th to the 56th day the samples lost some weight and their accumulated weight gain dropped to 2.6%. The final value of the average weight gain of the three samples was 2.9% at 84 days, which is considered to be low.

The immersion of the urethane grout samples in real-site refinery waste caused only a slight softening of the samples by the 28th day of testing. By then the color of the samples turned from white to black. No more changes were indicated after the 28th day.

- Reactivity Test of Urethane Grout With 25% Sodium Hydroxide

Three samples of urethane were tested for their reactivity with 25% sodium hydroxide. Each sample was cylindrical in shape, 25 mm in both diameter and thickness. The samples had an average weight increase of 3.6% following immersion in a sodium hydroxide bath for one day. No readings could be made on the 7th day or thereafter since by the 7th day the samples had totally disintegrated. Each sample reacted in a similar manner.

- Reactivity Test of Urethane Grout With Xylene

The reactivity of three standard size 25 mm diameter by 25 mm thick cylindrical samples of urethane was tested with xylene.

The three samples were placed in their respective xylene baths for 84 days. Weight measurements were taken at the standard elapsed times of 1, 7, 14, 28, 56, and 84 days. The results of the measurements on the three samples are plotted in Figure 153 as percent weight change versus time curves.

As can be observed on the test plots, the three samples gave very consistent test results. The overall trend of the results show a gradual weight loss throughout the tests. During the first 56 days, the three samples very gradually lost an average of 4.9% of their initial weight. Between the 56th and 84th day the rate of weight loss increased somewhat and the samples underwent an average 10% accumulated weight loss by the end of the testing period.

The immersion of the urethane grout samples in xylene transformed their consistency from rubbery to hard within 14 days. The samples remained hard until the end of their tests. Also, the samples turned to a light green color by the end of the test period.

In summary, the three samples gave very consistent results on xylene. The total decrease in weight of the three samples amounted to an average 10% accumulated weight loss. This is considered to be a medium low to medium weight loss. These three samples did not reach an equilibrium by the end of the test period, and it appears that had the tests been continued, more weight loss might have occurred.

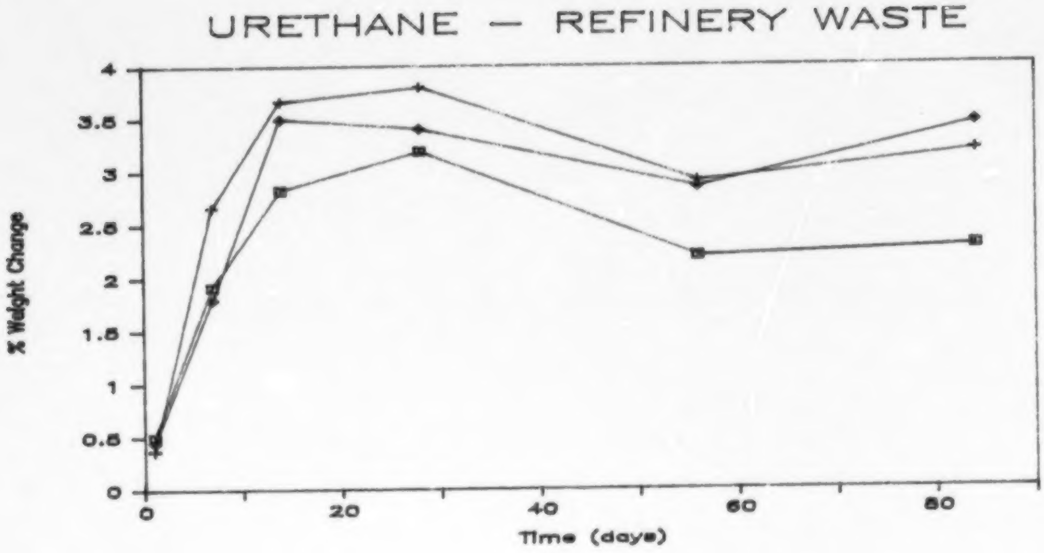


Figure 152. Percent weight change versus time plots for urethane grout samples immersed in real-site refinery waste.

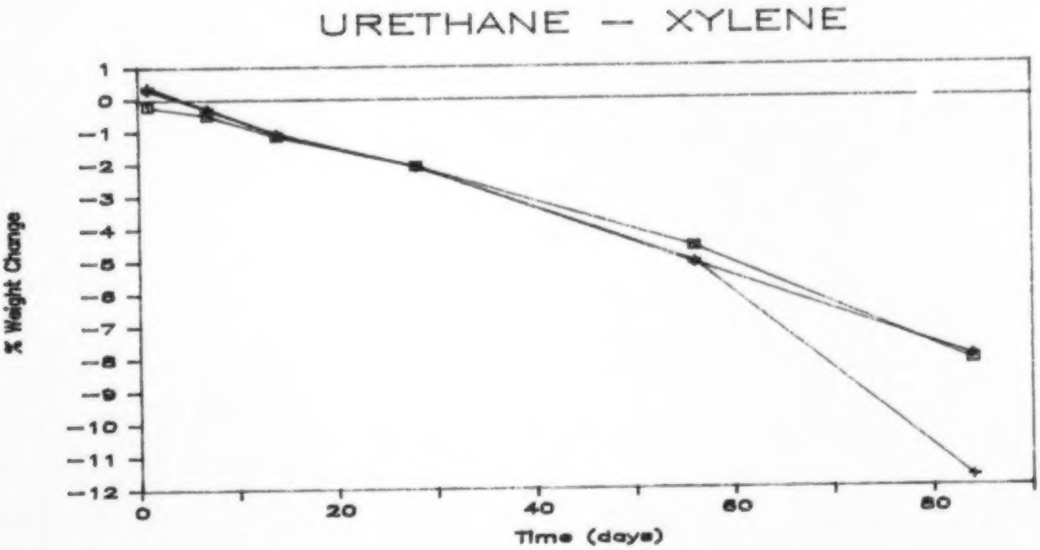


Figure 153. Percent weight change versus time plots for urethane grout samples immersed in xylene.

COMPARATIVE ANALYSIS OF PERMEABILITY AND REACTIVITY TEST RESULTS

As can be seen in the preceding sections, the two types of tests that were conducted on grouted soil samples were the permeability and reactivity tests. The main purpose of this project was to determine the baseline permeabilities of the various grouted samples with water, and the changes in their permeability when permeated with selected chemicals. For this, permeability tests were conducted on various grouted soil samples in triaxial type permeameters. This type of test requires special equipment, and is expensive and time consuming, but it provides the direct answer to the question: will the permeability of a selected grout be affected adversely by a given chemical waste.

In addition, reactivity tests were conducted on the various grouted samples. The purpose was to observe if a grouted sample would gain or lose weight when immersed in a selected chemical, and would its consistency also change in the process. This test is typically simpler, less expensive, and requires less complex equipment than the permeability test. In this section, the results from the two types of tests are compared and a scheme is proposed to allow the prediction of the permeability behavior of grouts with various chemicals from their behavior with the same chemicals in the reactivity test. It is proposed that with the presented correlations the choice of the most suitable grout for a site could possibly be made based on reactivity tests only, and these could be conducted at the site of the hazardous waste.

In the analysis of the reactivity tests on grouted samples, the following specific cases were observed:

- Case A: The test samples gained weight (the samples swelled)
- Case B: The test samples lost weight
  - Case B.1: The test samples spalled
  - Case B.2: The test samples shrank
    - Case B.2.a: The test samples shrank and hardened
    - Case B.2.b: The test samples shrank and softened
- Case C: The test samples initially gained weight but ultimately suffered a net weight loss
  - Case C.1: The test samples softened
  - Case C.2: The test samples hardened or remained hard
- Case D: The test samples initially lost weight but ultimately had a net weight gain
- Case E: The test samples initially gained large percentages of weight, but ultimately disintegrated.

The following sections describe the relationships between reactivity and permeability behavior that were observed.

Case A: The Test Samples Gained Weight (the Samples Swelled)

It was observed that if a reactivity test sample with a given chemical swelled and remained swollen throughout the test, then a corresponding permeability sample in a triaxial type permeameter, permeated with the same chemical, had a decrease in its permeability. As an explanation, it is postulated that the swelling grout was confined in the triaxial permeameter, so upon swelling it tended to reduce the size of the voids. This would result in reduced permeability, or at the least, in only small increases in the permeability of the samples.

The tests with the following grout-chemical combinations belong in this category:

urethane with aniline
urethane with real-site paint waste
urethane with real-site refinery waste
cement-bentonite (mix 1) with real-site paint waste
cement-bentonite (mix 1) with real-site refinery waste
cement-bentonite (mix 2) with aniline
cement-bentonite (mix 2) with 20% cupric sulfate

The acrylate grout samples with 100% ethylene glycol deviated from the above described behavior, in that they swelled, yet their permeability increased by approximately 2 orders of magnitude.

In summary, if a grout sample is tested in a given chemical by the standard reactivity tests and is found to increase in weight, then one may predict with reasonable certainty that when permeated by the same chemical, the permeability of the grout will probably decrease somewhat, or at worst, will increase minimally.

Case B.1: The Test Samples Lost Weight and Spalled

It was found that if a reactivity test sample, immersed in a given chemical, lost weight by the spalling off of its exterior layers, and at the same time the interior portion of the sample remained relatively intact, then a corresponding sample permeated with the same chemical in a triaxial type permeameter exhibited only a slightly, or moderately increased, permeability. It is believed that the portion of the sample which was first exposed and may have disintegrated would have an increased permeability, but the rest of the sample could still be unaffected. This would result initially in a slightly or moderately increased permeability for the whole sample, depending upon the degree of disintegration. The permeability of a sample may not be changed much until the whole sample, or a large part of it, has disintegrated.

The test of cement-bentonite (mix 2) grout with 4N hydrochloric acid supports the above described observations and belongs in this category.

In summary, if a grout sample is immersed in a given leachate in order to be tested by the standard reactivity procedure, and is found to lose weight by spalling while the consistency of the remaining part of the sample is unchanged, then one can predict with some certainty that the permeability of the grout will increase only moderately when permeated with the same leachate.

Case B.2.a: The Test Samples Lost Weight, Shrank, and Hardened

It was observed that if a reactivity sample shrank when immersed in a given chemical, and remained hard or became relatively hard in the process, then the corresponding triaxial permeability sample permeated by the same chemical exhibited increased permeability. The probable reason was that the grout in the triaxial sample also shrank, and since it was hard it probably also cracked, which opened extra voids and flow channels in the sample which allowed the increased flow. The tests with the following grout-chemical combinations support the above observations and belong in this category:

acrylate with 100% acetone
acrylate with 100% methanol
urethane with xylene
cement-bentonite (mix 1) with 100% acetone
cement-bentonite (mix 1) with 100% methanol

There were no exceptions to this behavior in this test series.

In summary, if a grout sample is tested in a selected chemical by the standard reactivity test, and is found to lose weight and also get hard or stay hard in the process, then one may predict with reasonable certainty that when the grout is permeated with the same chemical its permeability will increase significantly.

Case B.2.b: The Test Samples Lost Weight, Shrank, and Softened

It was observed that if a reactivity sample shrank while immersed in a given chemical, and also became soft, then the corresponding triaxial permeability sample subjected to the same chemical underwent a wide range of permeability increases. It is speculated that small increases occurred when the softening of a sample took place quickly, and large increases when the sample softened slowly. This can be explained by noting that if the reactivity sample shrank then the grout in the permeability sample also must have shrunk. So there probably developed extra void spaces in the soil sample that allowed increased flow through the sample. It is speculated that if the sample got soft early in the test then the seepage forces and the confining pressures tended to close the above voids and the permeability increases were only small to moderate. However, if the sample remained fairly hard over most of the test period, then the extra void spaces remained open for the greater part of the test and the permeability increases were large.

The tests with the following grout-chemical combinations exhibited these conditions:

acrylate with 4N hydrochloric acid
acrylate with xylene
urethane with 100% acetone

There were no exceptions to the above described behavior in the entire test series.

In summary, if a grout sample is immersed in a leachate and it gradually loses weight while it also becomes soft, then it is predicted that the permeability of the grout with the same chemical will increase. The magnitude of increase will be small if the grout softens quickly, and large otherwise.

Case C.1: The Test Samples Initially Gained Weight But Ultimately Suffered a Net Weight Loss, and Softened

It was found that if a reactivity grout sample, which was immersed in a given chemical, swelled at the beginning of the test, and later shrank, and in the process became soft, then a corresponding sample tested with the same chemical in the triaxial type permeameter underwent only small changes in permeability. The reason was that the initial swelling blocked the flow of the chemical, but once the softened grout began to shrink, the soft sample was deformed by the seepage forces and the confining pressure. The developing voids and shrinkage cracks were thus kept closed restricting the flow to a low level. However, it is believed that the time and the degree of softening of the grout has an effect on the permeability, namely the quicker the grout softens, the smaller the increase in permeability that will take place.

The tests with the following grout-chemical combinations belong in this category:

acrylate with real-site paint waste
acrylate with real-site refinery waste
acrylate with 25% sodium hydroxide
urethane with 100% methanol
cement-bentonite (mix 1) with xylene (no information available on softening)
cement bentonite (mix 2) with sodium hydroxide

There were no exceptions to this behavior in the test series.

In summary, if a grout sample is tested in a given leachate by the standard reactivity test and it is found to gain weight during the early days of testing, then lose weight as the tests proceeds and get soft in the process, then one may predict with reasonable certainty that the permeability of the same grout will be affected only minimally when permeated with the same leachate.

Case C.2: The Test Samples Initially Gained Weight But Ultimately Suffered A Net Weight Loss, and Hardened or Remained Hard

It was observed that if a reactivity grout sample, which was immersed in a given chemical, swelled during the beginning segment of the test and later shrank, and during the test period it remained or became hard, then a triaxial permeability sample made of the same grout and tested with the same chemical underwent moderately high increases in its permeability. The reason was that in the shrinkage stage the sample was hard and the confining pressure could not keep the developing voids and cracks from opening up. Thus the flow through the sample had to increase. The only grout-chemical combination in the test matrix which exhibited this condition was the acrylate grout with 20% cupric sulfate.

In summary, if a selected grout sample is tested in a chemical according to the standard reactivity test procedure, and is found to gain weight in the early stages of testing and lose weight in the later stages, and becomes or remains hard during the test, then it can be predicted with reasonable certainty that the permeability of the grout will increase considerably when permeated by the same chemical.

Case D: The Test Samples Initially Lost Weight But Ultimately Had a Net Weight Gain

It was found that if a reactivity sample in a selected chemical initially exhibited a net weight loss, that is, it shrank, and some time later in the test it had a net gain in weight with or without softening, then a corresponding sample in the triaxial type permeameter underwent moderately high to high increases in permeability with the same chemical. These increases were moderate if the sample softened in the initial stages of the test, and were mostly high if the sample remained hard, or became hard during the test. The reason is that in the initial stages the shrunken grout matrix in the sample allowed increased amounts of flow through the sample, especially if it was not softened, but the increase in permeability was mitigated by the swelling of the sample in the latter stages of the test (depending upon the amount of swelling and the degree of softening).

The following grout-chemical combinations exhibited the above described behavior:

acrylate grout with aniline
urethane grout with 20% cupric sulfate
urethane grout with 4N ethylene glycol
urethane grout with 4N hydrochloric acid

There were not exceptions to this behavior among the tests of this project.

In summary, if a grout sample, immersed in a chemical, exhibits an initial weight loss that is followed by a weight increase in the latter stages of the test, it is predicted that the same sample, permeated with the same chemical, would exhibit moderately high to high increases in permeability, depending on the duration of the shrunken stage versus that of the swelled phase, and the softness of the sample.

Case E: The Test Samples Initially Gained Large Percentages of Weight, But Ultimately Disintegrated

It was observed that if a reactivity sample, which was immersed in a chemical, underwent a large volume increase at the beginning of its testing and then totally disintegrated, then the corresponding triaxial permeability sample, tested with the same chemical, exhibited a large increase in its permeability. The explanation is that the grout mass was dissolved in both types of samples, and in the permeability test sample the resistance against flow was greatly reduced. The urethane grout sample with 25% sodium hydroxide was the only grout/chemical that exhibited this behavior.

From the practical point of view, if a grout sample is tested in a selected chemical by the standard reactivity test, and it is found to disintegrate within a short time period, then it can be predicted with reasonable certainty that if the grout is permeated with the same chemical, its permeability will increase greatly.

Table 13 summarizes the above comparison of permeability and reactivity test results. Within Table 13 is found the proposed scheme to predict changes in permeability of a grout based on the weight and consistency changes that it may undergo during its reactivity test.

TABLE 13. PREDICTED PERMEABILITY BEHAVIOR BASED ON REACTIVITY TEST RESULTS

WEIGHT/ VOLUME CHANGES CONSISTENCY CHANGES	VOLUME INCREASE/ WEIGHT GAIN	VOLUME DECREASE/ WEIGHT LOSS	WEIGHT LOSS BY SPALLING	INITIAL VOLUME INCREASE, LATER SHRINKAGE (INITIAL WEIGHT) GAIN, WEIGHT LOSS AS TEST PROCEEDS)	INITIAL VOLUME DECREASE, LATER VOLUME INCREASE (INITIAL WEIGHT LOSS, WEIGHT GAIN AS TEST PROCEEDS)
None			Moderate increase in permeability (Case B1)		
Remains hard or becomes hard		Permeability increases significantly (Case B.2.a)		Considerable increase in permeability (Case C.2)	Large increase in permeability (Case D)
Softens	Permeability decreases somewhat, or at worst, increases minimally (Case A)			Permeability affected minimally (Case C1)	
Softens quickly		Increase in permeability is small (Case B.2.b)			Moderate increase in permeability (Case D)
Softens slowly		Increase in permeability is large (Case B.2.b)			
Disintegrates	Permeability increases greatly (Case E)				

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